Coupled states cross sections for rotational excitation of H_2CO by He impact at interstellar temperatures

Barbara J. Garrison*

Department of Chemistry and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

William A. Lester, Jr.†

IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California 95193
(Received 24 September 1976)

Cross sections for rotational excitation of ortho formaldehyde due to collision with helium are computed following the coupled states (CS) formalism and compared with recent coupled channel (CC) results obtained employing the same *ab initio* configuration interaction intermolecular potential. The CS equations are integrated at 9 scattering energies between 25 and 95°K using a basis set of 16 ortho H_2CO states ($1 \leq j \leq 5$). The CS procedure with the orbital angular momentum quantum number l set equal to the total angular momentum J yields the correct order of magnitude for scattering cross sections. Qualitative differences are found, however, in the energy dependence of some inelastic transitions.

I. INTRODUCTION

During the past few years, considerable interest has developed around the anomalous absorption of interstellar formaldehyde. This absorption is anomalous because it predicts excitation temperatures for the 6 cm and 2 cm doublets of H_2CO lower than both the isotropic background temperature ($T_{iso} \approx 2.7$ °K) and the expected kinetic temperature ($10° \leq T_k \leq 20$ °K).[1] The most feasible model to explain this cooling is based on a collisional pump.[2] To test this collisional model, interaction energies obtained using extended basis set Hartree–Fock[3] and configuration interaction[4] methods were used to construct a potential energy surface which was subsequently employed in a coupled channel (CC) computation of scattering cross sections.[5] This rigorous study supported the collisional cooling mechanism of interstellar H_2CO.[6] In addition to serving as a validation of the collisional cooling mechanism, however, the cross sections computed in this study can serve as a standard for gauging the adequacy of more approximate and less time-consuming methods.

One such method that has demonstrated promise in applications to atom–diatom,[7–9] atom–linear polyatomic molecule,[9] and most recently to atom–symmetric top systems[10] is the coupled states (CS) procedure of McGuire and Kouri,[7] and of Pack.[11] A notable deficiency of the method that has been reported,[8(e)] is the inability to reliably describe systems with strong anisotropic interactions at long range. Because the CS method leads to significantly fewer equations, and therefore less computer time than the CC method, it is worthwhile to ascertain the utility of the CS method for an atom–asymmetric top system where there are accurate CC values for comparison. This is the purpose of the present study.

The remainder of this paper is organized as follows: Sec. II presents the CS scattering theory and Sec. III outlines the scope of the computations, cross section results, and related discussion. A summary of the study forms the content of Sec. IV.

II. COUPLED STATES THEORY OF ATOM-ASYMMETRIC TOP SCATTERING

As done in Ref. 5, we assume that the atom is a structureless projectile and the top is in a singlet state so that details associated with the coupling of spin angular momentum do not enter. (As in the treatment of atom–diatom systems, the extension to the inclusion of spin for both particles is straightforward.) Collision energies are assumed to be sufficiently low that vibrational and electronic excitations are not possible.

In the center of mass frame, the Hamiltonian for the atom–molecule system is

$$H = -\frac{\hbar^2}{2\mu} r^{-1} \frac{\partial^2}{\partial r^2} r + \frac{\mathbf{L}}{2\mu r^2} + H_{top} + V \,, \tag{1}$$

where the terms from left to right are the radial kinetic energy operator, the orbital angular momentum operator for relative motion, the asymmetric top Hamiltonian,[5] and the intermolecular potential. Here μ is the reduced mass of the total system, and r is the distance from the center of mass of the top to the atom. The orbital angular momentum is given by $\mathbf{L} = (\mathbf{J} - \mathbf{j})$, where $\mathbf{J}$ is the total angular momentum and $\mathbf{j}$ is the rotational angular momentum of the top.

The Schrödinger equation for the system is

$$(H - E_{tot}) \Psi^{JMj\Omega\tau} = 0 \,, \tag{2}$$

where E_{tot} is the total (relative kinetic plus internal) energy of the atom–asymmetric top system, M is the space fixed (SF) projection of J, and $j\Omega\tau$ labels the incident channel. Note that Ω is the projection of J along a body fixed axis and τ designates the energy levels of the top. Instead of coupling the rotational and orbital angular momenta as is usually done in the SF formulation, one may transform to a body fixed (BF) frame by rotating coordinate axes so that the new z axis is directed from the center of mass of the top to the atom.[12] The Euler angles $(\phi', \theta', 0)$ accomplish this rotation where the angles $(\theta'\phi')$ prescribe the orientation of the atom in the SF frame.

The effect of this rotation on $\Psi^{JMj\Omega\tau}$ has been discussed by Pack[11] and results in

$$\Psi^{JMj\Omega\tau} = \sum_{\Omega''=-J}^{J} D^{J}_{M\Omega''}(\phi', \theta', 0)^* \Psi^{Jj\Omega\tau}_{\Omega''}(\xi, \theta, \phi) , \tag{3}$$

where $D^{J}_{M\Omega''}(\phi', \theta', 0)^*$ are rotation matrix elements following the convention of Rose[13] and (ξ, θ, ϕ) are orientation angles of the asymmetric top in the BF frame. The function $\Psi^{Jj\Omega\tau}_{\Omega''}$ is further separated into a radial part and an angular part:

$$\Psi^{Jj\Omega\tau}_{\Omega''}(\xi, \theta, \phi) = \sum_{j''} \sum_{\tau''} r^{-1} G^{Jj\Omega\tau}_{j''\Omega''\tau''}(r) \phi^{j''\Omega''}_{\tau''}(\xi, \theta, \phi) , \tag{4}$$

where

$$\phi^{j''\Omega''}_{\tau''}(\xi, \theta, \phi) = \sum_{k''=-j''}^{j''} a^{j''}_{k''\tau''} (-1)^{\Omega''-k''} \times \left(\frac{2j''+1}{8\pi^2}\right)^{1/2} D^{j''}_{-\Omega''-k''}(\xi, \theta, \phi) . \tag{5}$$

Equation (5) is, of course, the expansion of the asymmetric top wavefunction (of energy $\epsilon_{j''\tau''}$) in terms of rotation matrix elements.

Substituting Eqs. (1) and (3)–(5) into Eq. (2), multiplying on the left by $(2\mu/\hbar^2)\phi^{j'\Omega'}_{\tau'}(\xi, \theta, \phi)^*$, and integrating over (ξ, θ, ϕ), one obtains the set of coupled equations

$$h^{j'}_{\Omega'\Omega'-1} G^{Jj\Omega\tau}_{j'\Omega'-1\tau'}(r) + h^{j'}_{\Omega'\Omega'} G^{Jj\Omega\tau}_{j'\Omega'\tau'}(r) + h^{j'}_{\Omega'\Omega'+1} G^{Jj\Omega\tau}_{j'\Omega'+1\tau'}(r) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{\tau''} \langle j'\Omega'\tau'; J | V | j''\Omega'\tau''; J \rangle G^{Jj\Omega\tau}_{j''\Omega'\tau''}(r) , \tag{6}$$

where

$$h^{j'}_{\Omega'\Omega'} = \frac{d^2}{dr^2} + k^2_{j'\tau'} - [J(J+1) + j'(j'+1) - 2\Omega'^2] r^{-2} , \tag{7}$$

$$h^{j'}_{\Omega'\Omega'\pm1} = \{[J(J+1) - \Omega'(\Omega'\pm1)] \times [j'(j'+1) - \Omega'(\Omega'\pm1)]\}^{1/2} r^{-2} , \tag{8}$$

and

$$k^2_{j'\tau'} = \frac{2\mu}{\hbar^2} (E_{\text{tot}} - \epsilon_{j'\tau'}) . \tag{9}$$

The coupling matrix elements of Eq. (6) are given by

$$\langle j'\Omega'\tau'; J | V | j''\Omega'\tau''; J \rangle = \int d\omega \phi^{j'\Omega'*}_{\tau'}(\xi, \theta, \phi) V(r, \theta, \phi) \phi^{j''\Omega''}_{\tau''}(\xi, \theta, \phi) . \tag{10}$$

To evaluate the coupling matrix elements, the interaction potential is written[5]

$$V(r, \theta, \phi) = \sum_{\lambda\nu} \left(\frac{4\pi}{2\lambda+1}\right)^{1/2} v_{\lambda\nu}(r) Y_{\lambda\nu}(-\theta, -\phi) = \sum_{\lambda\nu} v_{\lambda\nu}(r) D^{\lambda}_{0\nu}(0, \theta, \phi) . \tag{11}$$

Substituting Eq. (11) into Eq. (10) yields

$$\langle j'\Omega'\tau'; J | V | j''\Omega'\tau''; J \rangle = \sum_{k'=-j'}^{j'} \sum_{k''=-j''}^{j''} a^{j'}_{k'\tau'} a^{j''}_{k''\tau''} \sum_{\lambda} v_{\lambda, k'-k''}(r) \times (-)^{\Omega''+k''} [(2j'+1)(2j''+1)]^{1/2} \times \begin{pmatrix} j' & j'' & \lambda \\ \Omega' & -\Omega' & 0 \end{pmatrix} \begin{pmatrix} j' & j'' & \lambda \\ k' & -k'' & k''-k' \end{pmatrix} , \tag{12}$$

where ( ) denotes a 3-j symbol.[14] Unlike the SF formulation, no 6-j symbols appear here. As in the SF case, however, the coupling matrix elements are independent of M.

The expression for the degeneracy averaged cross section has been presented previously[11] and is

$$\sigma_{j'\tau'\to j\tau} = \frac{\pi}{k^2_{j\tau}(2j+1)} \sum_{J=0}^{\infty} (2J+1) \times \sum_{M=-j_<}^{j_<} \sum_{\Omega''=-j'_<}^{j'_<} |T^{J}_{j'\Omega'\tau'-jM\tau}|^2 , \tag{13}$$

where $j_<$ is the lesser of j and J, $j'_<$ is the lesser of j' and J, and

$$T^{J}_{j'\Omega'\tau'-jM\tau} = \delta_{j'j}\delta_{\Omega'M}\delta_{\tau'\tau} - S^{J}_{j'\Omega'\tau'-jM\tau} . \tag{14}$$

The BF formulation leads to the same number of coupled equations as the SF formulation, but the BF equations are more difficult to solve because the off-diagonal coupling terms [corresponding to Coriolis forces, see Eq. (8)] do not vanish asymptotically. The BF equations, however, lend themselves to approximations that significantly reduce the number of coupled channels.[15] In the CS method, one obtains this reduction by (a) neglecting the Coriolis interaction and (b) replacing $\mathbf{L}^2$ by $\hbar^2 l(l+1)$, where l is restricted to a single fixed value lying between $|J-j|$ and $J+j$. With these assumptions, the BF CC equations, i.e., Eq. (6), reduce to the CS equations:

$$\left(\frac{d^2}{dr^2} + k^2_{j'\tau'} + \frac{\hbar^2 l(l+1)}{r^2}\right) F^{Jj\Omega\tau}_{j'\Omega'\tau'}(r) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{\tau''} \langle j'\Omega'\tau'; J | V | j''\Omega'\tau''; J \rangle F^{Jj\Omega\tau}_{j''\Omega'\tau''}(r) , \tag{15}$$

where the coupling matrix elements are given by Eq. (12).

Comparing Eq. (15) with Eq. (6) shows the simplifications of the CS approach over, the exact BF CC equations, namely, (a) neglect of the Coriolis interaction as reflected in omission of the nondiagonal kinetic energy terms on the left-hand side of Eq. (6), and (b) use of the trivial centrifugal barrier term of Eq. (15) in place of the one of Eq. (7). Furthermore, we note the significant reduction obtained over the exact SF CC equations by the absence of a summation over l'', see Eq. (14) of Ref. 5.

At this point the CS equations are not completely specified because the value of l in the centrifugal barrier term has not been designated. With the notable exception of Kouri and McGuire's CS study of the Li^+-H_2 system[8(e)] in which cross sections computed with $l = |J-j|$ were found to yield the closest agreement with CC results, the common choice is the "average" value or $l = J$. In the present study, three specifications of l are investigated: $l = J$, $|J-j|$, and $J+j$.

Finally we note that in the CS method, the degeneracy averaged cross section takes the form

$$\sigma_{j\tau\to j'\tau'} = \frac{\pi}{k_{j\tau}^2(2j+1)} \sum_{J=0}^{\infty} (2J+1) \sum_{\Omega'=-\min(J,j',J)}^{\min(J,j',J)} |T_{j\Omega\tau,j'\Omega'\tau'}^{J}|^2 . \quad (16)$$

III. RESULTS AND DISCUSSION

To facilitate comparison with our previously computed CC cross sections,[5] the CS equations (6) are integrated at the same values of the total energy E_{tot} investigated in the CC study, omitting however, those energies (~ 20.2, 32.7, and 47.7 °K) at which resonances were found in the earlier study. Sixteen ortho H_2CO ($1 \le j \le 5$) states were included in the basis set leading to 16 coupled equations versus 62 obtained in the CC study. As in the CC computations, Gordon's method[16] was used to integrate the coupled equations.

Table I lists CS and[5] CC integral cross sections for all inelastic transitions studied. The transitions are specified both by the usual spectroscopic notation and numerically, in parentheses, with increasing energy proceeding from the ground 1_{11} state. Figure 1 presents some representative CS inelastic cross sections, plotted versus total energy, obtained using the three specifications of the centrifugal barrier term discussed in Sec. II. Although there is considerable variation in the energy dependence of the cross sections obtained using the three choices of l for $E_{tot} \lesssim 45$ °K, above this energy (which is above the region where the resonance structure is important[5]), setting $l=J$ provides the best agreement with CC results. The improvement of the CS method with increasing energy is discussed by Kouri *et al.*[17] We note, however, that basis set convergence

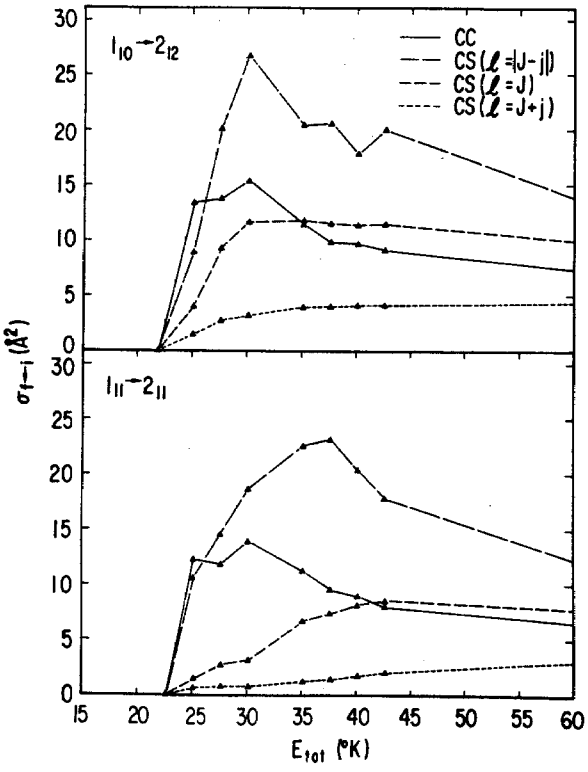

FIG. 1. Comparison of CC and CS inelastic cross sections for transitions $1_{10}(2) \to 2_{12}(3)$ and $1_{11}(1) \to 2_{11}(4)$.

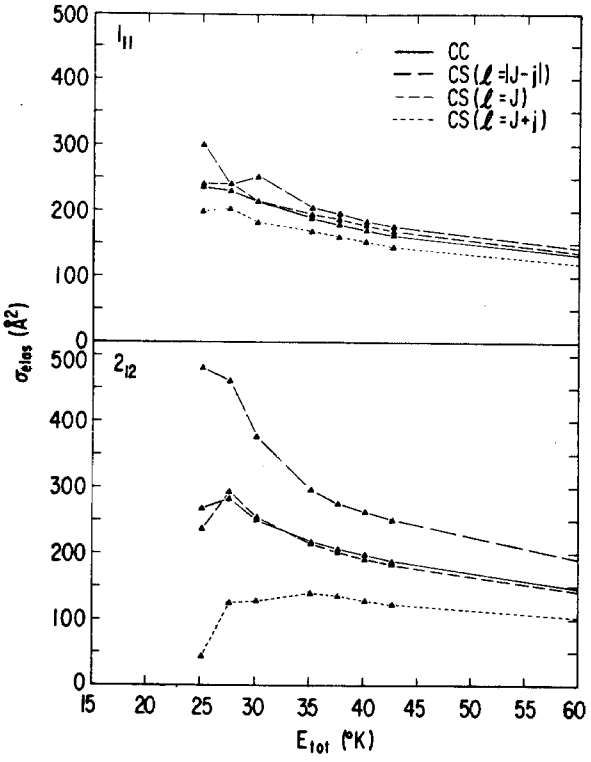

FIG. 2. Comparison of CC and CS elastic cross sections for states $1_{11}(1)$ and $2_{12}(3)$.

was not confirmed at these higher energies which correspond to the high energy region in the Boltzmann distribution needed in determining cooling rates; see below.

Table II presents elastic cross sections for the lowest three rotational doublets of ortho H_2CO, and Fig. 2 displays the energy dependence for the first $1_{11}(1)$ and third $2_{12}(3)$ states. Again the $l=J$ CS energy dependence is found to be in best accord with the CC result and, in contrast to the inelastic cross section behavior, agrees well over the entire energy range explored.

Even though CS cross sections display sizable differences from CC ones, it is worthwhile forming the CS rate constants for use in the equations of statistical equilibrium to test for cooling of the 6 cm (T_{12}) and 2 cm (T_{34}) doublets.[18] We solved the equations of statistical equilibrium assuming a kinetic temperature of 15 °K and helium concentrations $n(\text{cm}^{-3})$ in the range $10^2 \le n \le 10^6$. As may be seen in Fig. 3, both T_{12} and T_{34} drop below the 2.7 °K background temperature, i.e., cooling is obtained for each of the CS specifications of the barrier term used. This lack of sensitivity of the cooling curves to the alternative choices of barrier term is readily understood from our CC study, which established that the rate constant ratios k_{23}/k_{14} and k_{25}/k_{16} are the determiners of cooling. Therefore, in view of the differences between the best CS prescription of the barrier term ($l=J$) and CC results, we conclude that the results of a CS study could not serve as a definitive indicator of cooling in the present system without the availability of CC results to serve as a guide.

TABLE I. Comparison of coupled channel and coupled states inelastic cross sections.[a]

	E_{tot}(° K)								
	25.1668	27.6668	30.1668	35.1668	37.6668	40.1668	42.6668	70.1668	95.1668
$1_{11}(1) \rightarrow 1_{10}(2)$	25.6	17.8	15.1	12.3	11.5	11.1	10.1	7.6	6.6
	26.9	23.8	10.1	12.2	12.0	10.6	7.4	6.0	5.4
	27.3	25.7	18.0	14.1	12.3	11.7	10.7	6.9	5.9
	24.7	21.3	18.9	15.1	13.7	13.0	12.2	8.9	7.6
$1_{11}(1) \rightarrow 2_{12}(3)$	22.7	23.3	23.3	20.2	18.1	17.1	16.7	10.5	8.5
	35.1	34.9	29.2	30.5	26.0	24.7	25.4	11.8	8.7
	17.4	19.6	20.9	19.9	18.0	17.3	17.2	11.3	8.8
	6.3	8.7	9.7	10.4	10.1	10.0	9.9	8.4	7.3
$1_{11}(1) \rightarrow 2_{11}(4)$	12.2	11.8	13.9	11.2	9.5	8.9	8.0	5.7	5.2
	10.5	14.5	18.6	22.6	23.1	20.4	17.8	8.9	4.7
	1.5	2.7	3.1	6.7	7.3	8.1	8.5	7.3	5.5
	0.6	0.8	0.8	1.2	1.4	1.7	2.0	3.7	4.0
$1_{11}(1) \rightarrow 3_{13}(5)$				4.1	5.4	6.3	6.4	5.4	4.6
				8.2	10.2	11.4	12.7	8.7	4.2
				2.9	4.0	4.3	4.4	4.3	4.0
				0.5	1.1	1.5	1.6	1.9	1.9
$1_{11}(1) \rightarrow 3_{12}(6)$				0.3	0.6	0.8	1.2	0.9	1.3
				0.5	0.8	0.8	1.4	1.0	1.4
				0.2	0.3	0.3	0.3	0.7	1.1
				0.1	0.2	0.2	0.2	0.6	0.9
$1_{10}(2) \rightarrow 2_{12}(3)$	13.4	13.8	15.4	11.5	9.9	9.7	9.2	6.3	5.4
	8.9	20.1	26.8	20.5	20.6	17.8	20.0	10.2	5.2
	4.0	9.3	11.6	11.8	11.6	11.4	11.5	9.0	6.6
	1.5	2.7	3.2	4.0	4.0	4.1	4.2	4.5	4.3
$1_{10}(2) \rightarrow 2_{11}(4)$	14.2	13.3	16.0	14.3	12.4	11.6	10.3	8.4	7.8
	12.2	8.4	10.7	13.2	14.1	12.7	8.2	8.5	7.6
	10.2	8.9	7.8	9.2	8.7	8.7	8.1	7.4	7.0
	5.2	6.4	5.1	5.4	5.4	5.3	5.6	6.1	6.3
$1_{10}(2) \rightarrow 3_{13}(5)$				7.6	8.6	7.6	7.2	4.7	3.4
				12.0	15.0	13.0	13.2	8.5	5.3
				3.8	5.8	6.3	6.3	4.9	3.7
				0.4	1.1	1.7	2.0	2.0	1.6
$1_{10}(2) \rightarrow 3_{12}(6)$				1.6	2.4	2.6	3.7	4.5	4.3
				4.1	7.2	6.0	7.5	7.8	3.9
				0.9	1.1	1.0	1.1	3.2	3.6
				0.3	1.0	0.9	1.1	1.9	2.4
$2_{12}(3) \rightarrow 2_{11}(4)$	24.8	19.4	19.9	13.1	10.4	8.4	7.1	3.5	2.8
	42.1	45.9	40.4	22.6	18.7	14.2	11.2	3.8	2.8
	22.3	27.1	21.1	12.9	11.1	9.5	8.4	3.9	2.9
	6.4	12.6	8.0	6.5	5.7	5.1	4.7	3.1	2.7
$2_{12}(3) \rightarrow 3_{13}(5)$				11.9	13.3	13.3	12.9	11.6	11.1
				23.4	26.7	25.7	21.6	16.8	14.3
				9.7	12.6	13.0	12.4	11.7	11.0
				1.6	3.5	4.3	4.9	6.9	7.5
$2_{12}(3) \rightarrow 3_{12}(6)$				2.1	3.3	3.7	3.7	3.4	3.1
				3.3	4.0	4.1	3.7	5.9	3.3
				1.4	2.0	2.3	2.1	2.7	2.8
				0.1	0.2	0.7	0.9	1.6	1.9
$2_{11}(4) \rightarrow 3_{13}(5)$				7.1	7.9	6.9	7.3	3.7	2.8
				11.2	13.4	12.6	14.6	6.7	2.4
				4.4	5.2	5.5	5.7	4.1	3.2
				0.4	0.9	1.4	1.7	2.2	2.0
$2_{11}(4) \rightarrow 3_{12}(6)$				8.2	11.5	12.1	10.4	9.5	8.2
				18.9	21.5	18.6	15.9	12.2	9.3
				6.1	10.8	10.4	10.1	8.9	7.6
				0.4	1.8	2.9	3.7	5.3	5.6
$3_{13}(5) \rightarrow 3_{12}(6)$				9.6	10.2	8.8	9.2	2.8	2.1
				34.8	24.9	20.9	19.9	4.2	2.5
				16.1	12.2	9.4	7.7	3.0	2.1
				1.0	1.2	0.6	1.3	1.6	1.5

[a]Order of entries in the table: CC, CS($l = |J-j|$), CS($l=j$), and CS($l=J+j$). Cross sections in Å^2.

TABLE II. Comparison of coupled channel and coupled state elastic cross sections.[a]

	E_{tot}(°K)								
	25.1668	27.6668	30.1668	35.1668	37.6668	40.1668	42.6668	70.1668	95.1668
$1_{11}(1)$	235	229	213	189	179	170	163	115	93
	300	239	252	205	196	184	176	125	88
	241	241	215	194	187	178	169	118	88
	199	202	182	169	160	153	145	103	82
$1_{10}(2)$	257	241	231	194	182	174	167	115	93
	342	298	302	230	200	196	185	123	88
	242	236	220	204	194	185	177	118	88
	198	197	186	171	161	155	148	106	83
$2_{12}(3)$	267	282	249	217	205	197	186	122	96
	480	460	375	296	274	262	249	154	97
	236	292	253	214	201	190	182	121	93
	43	124	127	138	134	127	122	89	73
$2_{11}(4)$	308	306	263	228	211	204	195	124	97
	596	525	409	313	278	268	255	156	99
	257	319	289	244	221	207	198	126	96
	33	114	140	156	151	143	136	94	76
$3_{13}(5)$				289	277	255	244	135	103
				743	561	481	448	197	114
				252	263	239	233	131	101
				7	40	50	71	75	64
$3_{12}(6)$				253	288	293	281	142	106
				969	696	580	538	210	121
				176	282	266	266	142	107
				4	28	43	67	84	69

[a]Order of entries in the table: CC, CS($l=|J-j|$), CS($l=J$), and CS($l=J+j$). Cross sections in Å^2.

IV. SUMMARY

The coupled channel (CC) equations for rotational excitation of a structureless projectile by a spinless asymmetric top are derived in a body fixed frame. The coupled states (CS) approximation of McGuire and Kouri and of Pack is obtained from the exact CC equations and applied to the scattering of ortho H_2CO by He at interstellar temperatures using three specifications of the centrifugal barrier term of the CS formalism: $l=J+j$, J, and $|J-j|$.

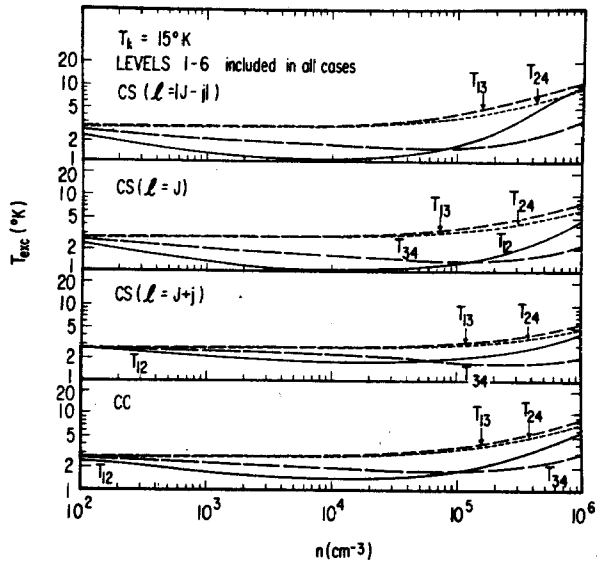

FIG. 3. Excitation temperatures as a function of He density for each of the CS schemes and the CC method.

For the present system, the choice $l=J$ is found to provide the best agreement with CC computed cross sections for both elastic and inelastic transitions. However, qualitative differences between this best CS choice and CC cross sections are obtained for inelastic cross sections. Cooling of both the 6 cm and 2 cm rotational doublets of ortho H_2CO is found using CS rate constants computed using each of the three specifications of the centrifugal barrier term. Thus the details of the inelastic cross sections are not important. Rather, as discussed in Ref. 5, it is ratios of inelastic rates which are the determiners of cooling, and these ratios are consistent with CC values.

ACKNOWLEDGMENT

One of us (B. J. G) is indebted to Professor W. H. Miller of the Department of Chemistry, University of California, Berkeley for helpful discussions, support, and encouragement during the course of this study.

*Visiting scientist at IBM Research Laboratory under a joint study agreement between the IBM Corporation and Lawrence Berkeley Laboratory. Present address: Department of Chemistry, Purdue University, West Lafayette, IN 47907.

†Research supported in part by the U. S. Office of Naval Research Contract No. N00014-72-C-0244.

[1](a) P. Palmer, B. Zuckerman, D. Buhl, and L. E. Snyder,

Astrophys. J. 156, L147 (1969); (b) N. H. Dieter, Astrophys. J. 183, 449 (1973); (c) Y. K. Minn and J. M. Greenberg, Astron. Astrophys. 22, 13 (1973); (d) N. J. Evans, II, A. C. Cheung and R. M. Sloanaker, Astrophys. J. 159, L9 (1970); (e) N. J. Evans. II, Ph. D. Thesis, University of California, Berkeley, 1973; (f) N. J. Evans, II, B. Zuckerman, G. Morris, and T. Sato, Astrophys. J. 196, 433 (1975).

[2]C. H. Townes and A. C. Cheung, Astrophys. J. 157, L103 (1969).

[3]B. J. Garrison, W. A. Lester, Jr., and H. F. Schaefer, III, J. Chem. Phys. 63, 1449 (1975).

[4]B. J. Garrison, W. A. Lester, Jr., P. Siegbahn, and H. F. Schaefer, III, J. Chem. Phys. 63, 4167 (1975).

[5]B. J. Garrison, W. A. Lester, Jr., and W. H. Miller, J. Chem. Phys. 65, 2193 (1976).

[6]B. J. Garrison, W. A. Lester, Jr., W. H. Miller, and S. Green, Astrophys. J. 200, L175 (1975).

[7](a) P. McGuire and D. J. Kouri, J. Chem. Phys. 60, 2488 (1974); (b) P. McGuire, Chem. Phys. Lett. 23, 575 (1973).

[8](a) P. McGuire, J. Chem. Phys. 62, 525 (1975); (b) P. McGuire, Chem. Phys. 8, 231 (1975); (c) M. H. Alexander and P. McGuire, Chem. Phys. 12, 31 (1976). (d) P. McGuire and H. Krüger, J. Chem. Phys. 63, 1090 (1975); (e) D. J. Kouri and P. McGuire, Chem. Phys. Lett. 29, 414 (1974); (f) S. -I. Chu and A. Dalgarno, Proc. R. Soc. A 342, 191 (1975); (g) S. -I. Chu and A. Dalgarno, J. Chem. Phys. 63, 2115 (1975).

[9]P. McGuire, Chem. Phys. 13, 81 (1976).

[10]S. Green, J. Chem. Phys. 64, 3463 (1976).

[11]R. T Pack, J. Chem. Phys. 60, 633 (1974).

[12]Note that this specification of the body fixed frame differs from the usual spectroscopic choice in which the z axis is chosen to lie along a principal axis of the top.

[13]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[14]M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j Symbols* (Technology Press, Cambridge, Mass., 1959).

[15]Decoupling methods in a SF frame have been discussed by (a) D. Secrest, J. Chem. Phys. 62, 710 (1965); (b) R. B. Walker and J. C. Light, Chem. Phys. 7, 84 (1975); (c) H. Rabitz, J. Chem. Phys. 63, 5208 (1975).

[16](a) R. G. Gordon, J. Chem. Phys. 51, 14 (1969). (b) Meth. Comp. Phys. 10, 81 (1971); (c) Program 187 Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

[17]D. J. Kouri, T. Heil, and Y. Shimoni, J. Chem. Phys. 65, 1462 (1976).

[18]See Ref. 5 for a discussion of the equations of statistical equilibrium.