Coupled-channel study of rotational excitation of a rigid asymmetric top by atom impact: (H_2CO,He) at interstellar temperatures

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A quantum mechanical scattering study is carried out to test a collisional pumping model for cooling the 6 and 2 cm doublets of interstellar formaldehyde. The Arthurs and Dalgarno formalism is extended to the collision of an s-state atom with a rigid asymmetric top molecule and applied to rotational excitation of *ortho* formaldehyde by helium impact. Using a previously determined configuration interaction potential energy surface, the coupled-channel (CC) equations are integrated at 12 scattering energies between 20 and 95°K. Up to 16 *ortho* formaldehyde states, yielding a maximum of 62 CC equations, are retained to test convergence of computed cross sections. Resonance structure is obtained at ~20.2, 32.7, and 47.7°K. The computed inelastic cross sections are averaged over a Maxwell–Boltzmann distribution and the resultant rates used to solve the equations of statistical equilibrium for the relative populations. The 6 and 2 cm doublets are found to be cooled *only* upon inclusion of the $j = 3$ doublet.

I. INTRODUCTION

During the past few years, considerable interest has developed around observations of anomalous absorption in interstellar formaldehyde. This absorption is "anomalous" because it is seen toward dark clouds, implying an excitation temperature for two rotational states lower than either the background radiation temperature (~2.7 °K) or the expected kinetic temperature (10–20 °K). These observations are quite common in the interstellar medium and are seen in (1) the $1_{10} - 1_{11}$ (6 cm) transition of H_2CO,[1-3] (2) the $2_{11} - 2_{12}$ (2 cm) transition of H_2CO,[4-6] and (3) the $1_{10} - 1_{11}$ transition of the isotope $H_2{}^{13}CO$.[6]

To obtain such low excitation temperatures requires a nonthermal cooling mechanism. A number of pumping models have been proposed that involve transitions to higher rotational states of H_2CO followed by radiative decay. The pump or force causing the excitations has been variously suggested as being due to collisions[7] or to radiation at millimeter,[8,9] infrared,[10] and ultraviolet[11] wavelengths. Evans *et al.*[6] have recently given a convincing discussion which indicates that the collisional pump is the only model that accounts for all the observations and satisfies necessary criteria.

Since the collisional pump appears to be the key to understanding interstellar cooling of H_2CO, several workers have attempted to verify this model theoretically by determining the appropriate rotational cross sections. The validity of these studies is limited however, due to the use of approximate interaction potentials (hard[7] or soft sphere),[5,12,13] approximate dynamics (classical[7] or semiclassical[12] theory), and inappropriate approximations (Born[6] or sudden[14]).

In the present study the collisional pumping mechanism is investigated employing rigorous quantum mechanical calculations. The Arthurs and Dalgarno[15] coupled-channel (CC) formalism is extended to treat scattering of an asymmetric top by a structureless atom. Using a previously reported *ab initio* intermolecular potential[16,17] between H_2CO and He, the CC equations are integrated to yield rotational cross sections. Collisional rates are then determined from these cross sections and used to solve the equations of statistical equilibrium whose solutions permit one to ascertain the validity of the collisional pump as a mechanism for the cooling of interstellar H_2CO.[18] For these calculations, the most probable scatterer H_2 is replaced by He to reduce the scope of the computations. It is anticipated that the main conclusions of this study will not be seriously altered by this choice of scattering particle.

It should be noted that beam maser measurements[19] of rotational relaxation of H_2CO by collision with He and other gases and also microwave pressure broadening experiments[20] on the H_2CO–He system have been carried out at room temperature. Owing to the large disparity in collision energies between the present theoretical results and these two sets of measurements, a critical theory–experiment comparison is not obtainable.

The remainder of the paper is organized as follows. Section II discusses the properties of asymmetric top wavefunctions required for development of the CC scattering equations presented in Sec. III. Sec. IV describes the interaction potential and Sec. V outlines the scope of the scattering calculations and presents the

cross section results. The use of these cross sections to test the collisional pumping mechanism is described in Sec. VI followed by a summary of the study in Sec. VII.

II. ASYMMETRIC TOP

Before treating the scattering of an asymmetric top by an atom, it is useful to summarize the properties of the asymmetric top wavefunctions. An excellent detailed discussion is given by Davydov.[21]

It is convenient to define two coordinate systems: (1) a space fixed (SF) frame denoted by primes and (2) a body fixed (BF) frame (unprimed) attached to the center of mass of the top. The BF axes are taken to be coincident with the principal axes of the top. The orientation of the BF axes with respect to the SF axes is given by the three Euler angles $(\alpha\beta\gamma)$.[22]

The rotational Hamiltonian of the top is

$$H=\frac{1}{2}\left(\frac{J_x^2}{I_x}+\frac{J_y^2}{I_y}+\frac{J_z^2}{I_z}\right) \tag{1}$$

$$=AJ^2+(B-A)J_y^2+(C-A)J_z^2 . \tag{2}$$

Here J^2 is the square of the angular momentum operator J, J_i $(i=x,y,z)$ are the components of J along the BF axes, I_i are the principal moments of inertia, and $A=1/2I_x$, $B=1/2I_y$, and $C=1/2I_z$ are the rotational constants. To solve the Schrödinger equation for the Hamiltonian of Eq. (2), it is convenient to expand the asymmetric top wavefunction in a basis set of symmetric top (where $I_x=I_y$) wavefunctions, ψ_{jmjk}. The asymmetric top wavefunction is therefore expanded as

$$\phi_\tau^{jm_j}(\alpha\beta\gamma)=\sum_{k=-j}^{j} a_{k\tau}^j\psi_{jmjk}(\alpha\beta\gamma) , \tag{3}$$

where

$$\psi_{jmjk}(\alpha\beta\gamma)=\sqrt{\frac{2j+1}{8\pi^2}}D_{mjk}^{j\,*}(\alpha\beta\gamma) . \tag{4}$$

Here $D_{mjk}^j(\alpha\beta\gamma)$ is an element of the rotation matrix[22]; the $a_{k\tau}^j$ are expansion coefficients (to be determined); $j(j+1)\hbar^2$, $m_j\hbar$ $(|m_j|\le j)$, and $k\hbar$ $(|k|\le j)$ are the eigenvalues of J^2, $J_{z'}$ (SF projection), and J_z (BF projection) respectively; and τ labels the asymmetric top eigenfunctions (see below). Note that J^2 and $J_{z'}$ are conserved for both the symmetric and asymmetric top, while J_z is conserved only for the *symmetric* top. The fact that J_z is not conserved results in mixing of the $(2j+1)$ different values of k corresponding to a given (j,m_j) to form $(2j+1)$ states of the asymmetric top. These asymmetric top states are labeled by an index τ as indicated above.

Substitution of Eq. (3) into Eq. (2) leads to

$$\sum_k a_{k\tau}^j\{\langle\psi_{jm_jk'}|H|\psi_{jm_jk}\rangle-\epsilon_{j\tau}\delta_{k'k}\}=0 \tag{5}$$

for $(2j+1)$ values of τ. The matrix elements of H over the symmetric top wavefunctions can be found in Davydov.[22]

The $(2j+1)$ equations given by Eq. (5) can be simplified by employing the symmetry properties of the Hamiltonian. The Hamiltonian is invariant under the coordinate transformations: (1) identity transformation, (2) $x\to -x$, (3) $y\to -y$, and (4) $z\to -z$. These transformations form a representation of the Klein Four Group, which has four one-dimensional irreducible representations. By transforming the basis of symmetric top wavefunctions to a set of symmetry adapted functions, which transform according to the irreducible representations of the four group, the Hamiltonian matrix of Eq. (5) becomes block diagonal, thus decoupling the system of Eqs. (5) into four smaller systems. The four classes of symmetry adapted functions χ, are

$$\chi_{ks}^{\text{odd}}=\frac{1}{\sqrt{2}}[\psi_{jm_jk}+(-)^s\psi_{jm_j-k}],\quad k \text{ odd},\ s=0 \text{ or } 1 , \tag{6a}$$

$$\chi_{ks}^{\text{even}}=\frac{1}{\sqrt{2(1+\delta_{0k})}}[\psi_{jm_jk}+(-)^s\psi_{jm_j-k}],\quad k \text{ even},\ s=0 \text{ or } 1. \tag{6b}$$

Note that there are four types of functions (k is odd *or* even and $s=0$ or 1), each of which transforms according to a different irreducible representation. Equation (3) can now be restricted to sums over a single class of symmetry adapted functions,

$$\phi_\tau^{jm_j}=\sum_{k=0\,(1)}^{\text{even (odd)}} b_{k\tau}^j\chi_{ks}$$

where the state index τ now also implies odd *or* even values of k and a specific value of s (0 or 1). Equations (5) therefore reduce to four smaller systems of equations of the form

$$\sum_{k=0\,(1)}^{\text{even (odd)}} b_{k\tau}^j\{\langle\chi_{k's}|H|\chi_{ks}\rangle-\epsilon_{j\tau}\delta_{k'k}\}=0 . \tag{7}$$

These sets of equations can be solved by standard techniques in linear algebra to yield the eigenvalues $\epsilon_{j\tau}$ and expansion coefficients $b_{k\tau}^j$ of the asymmetric top.

The four coordinate transformations described above do not represent all of the symmetry properties of the asymmetric top Hamiltonian. The Hamiltonian also possesses inversion symmetry (simultaneous inversion of the x, y, and z coordinates), thus the full group of the top is $D_{2h}=D_2\otimes i$. (Here D_2 is a realization for the four group and i represents the inversion group.) In Sec. III this additional symmetry is used to simplify the CC scattering equations. Note further that

$$F\phi_\tau^{jm_j}=(-)^{j+k+s}\phi_\tau^{jm_j} , \tag{8}$$

where F is the inversion operator. Hence the symmetry adapted functions of Eq. (6) are necessarily symmetry adapted functions of the larger group D_{2h}.

For H_2CO there is a further symmetry owing to the interchange of the identical H nuclei that results in ortho (symmetric) and para (antisymmetric) couplings of nuclear spins. Since there is no interaction that couples nuclear spin states of different symmetry during collisions with He, ortho and para H_2CO can be treated separately. The astrophysical observations of interest in this study are of ortho H_2CO; therefore only ortho states need be included in the scattering calculations. Since the H nuclei are Fermions, the total wavefunction must be antisymmetric under their interchange.

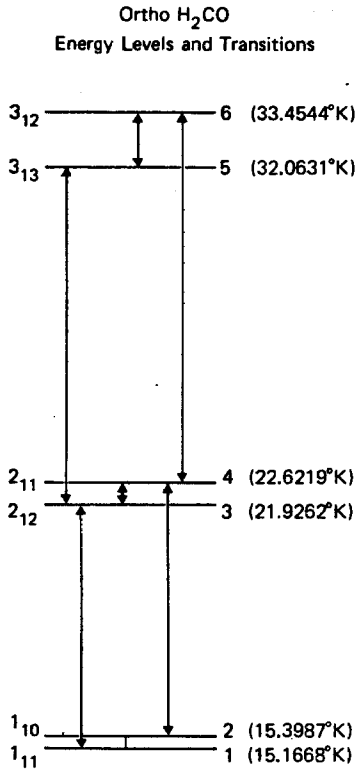

FIG. 1. Energy level diagram for ortho H_2CO with the dipole allowed transitions indicated.

The nuclear wavefunction is symmetric; therefore the rotational wavefunctions must be antisymmetric. Letting P be the operator that interchanges H nuclei then

$$P\phi_\tau^{jm_j} = (-)^k \phi_\tau^{jm_j} , \tag{9}$$

where again τ implies odd *or* even values of k. Since $\phi_\tau^{jm_j}$ must be antisymmetric for ortho H_2CO, Eq. (9) implies that only states with k *odd* [i.e., functions given by Eq. (6a)] are required in this study.

Using the rotational constants of Oka[23] ($A = 38\,835$ MHz, $B = 34\,003$ MHz, and $C = 282\,029$ MHz) to evaluate Hamiltonian matrix elements, the energy levels of ortho H_2CO were obtained from the solution of Eq. (7). These energy levels accompanied by two labeling schemes are given in Fig. 1. For the lower (upper) state of each doublet, $s = 1$ (0).

III. THEORY OF ATOM-MOLECULE SCATTERING

In this section the Arthurs and Dalgarno[15] (AD) coupled-channel (CC) formulation is extended to the scattering of an asymmetric top by an atom. For simplicity the atom is assumed spherical (^1S state) and the top is also taken to be in a singlet state so that details associated with the coupling of spin angular momentum are avoided. Collision energies are assumed to be sufficiently low that vibrational and electronic excitation is not possible.

The Hamiltonian of the total system (top plus atom) in center of mass coordinates is

$$H = (-\hbar^2/2\mu)\nabla_r^2 + H_{\rm int}(\hat{R}') + V(\mathbf{r}, \hat{R}') , \tag{10}$$

where the terms from left to right are the kinetic energy operator for relative motion, the rotational Hamiltonian [Eq. (2)] of the top, and the intermolecular potential. Here μ is the reduced mass of the total system, $\mathbf{r} \equiv (r, \theta', \phi')$ is the position of the atom in a space fixed (SF) frame and $\hat{R}' \equiv (\alpha\beta\gamma)$ is the orientation of the top in the SF frame.

An expansion method is used to solve the Schrödinger equation

$$(H - E_{\rm tot})\Psi = 0 . \tag{11}$$

The total angular momentum J and its SF z' projection $J_{z'} = M$ are conserved in this system. AD found it convenient to couple the rotational angular momentum j of the top and the relative orbital angular momentum l to form eigenfunctions of $J(=j+l)$ and $J_{z'}$. Following AD, the angular dependences are basis-set expanded, i.e., the wavefunction is written

$$\Psi_{jl\tau}^{JM}(\mathbf{r}, \hat{R}') = \sum_{j'l'\tau'} \frac{1}{r} u_{j'l'\tau',jl\tau}^{J}(r)\, \mathcal{Y}_{j'l'\tau'}^{JM}(\hat{r}', \hat{R}') , \tag{12}$$

where

$$\mathcal{Y}_{jl\tau}^{JM}(\hat{r}', \hat{R}') = \sum_{m_j=-j}^{j} \sum_{m_l=-l}^{l} C(jlJ; m_j m_l M) \times Y_{lm_l}(\hat{r}')\phi_\tau^{jm_j}(\hat{R}') . \tag{13}$$

Here $C(jlJ; m_j m_l M)$ is a Clebsch–Gordan coefficient,[22] $Y_{lm_l}(\hat{r}')$ is a spherical harmonic describing the relative angular momentum of the colliding system and $\phi_\tau^{jm_j}(\hat{R}')$ is the asymmetric top function of Eq. (3). Substituting Eqs. (10), (12), and (13) into Eq. (11), multiplying on the left by $\mathcal{Y}_{j''l''\tau''}^{JM*}$, integrating over $\hat{r}'$ and $\hat{R}'$, and making use of orthonormality relations,[22] yields the CC equations for the radial functions

$$\left[\frac{d^2}{dr^2} - \frac{l'(l'+1)}{r^2} + k_{j'\tau'}^2\right] u_{j'l'\tau',jl\tau}^{J}(r) = \frac{2\mu}{\hbar^2} \sum_{j''} \sum_{l''} \sum_{\tau''} \langle j'l'\tau'; J | V | j''l''\tau''; J\rangle\, u_{j''l''\tau'',jl\tau}^{J}(r) , \tag{14}$$

where

$$k_{j'\tau'}^2 = 2\mu(E_{\rm tot} - \epsilon_{j'\tau'})/\hbar^2 . \tag{15}$$

The coupling matrix elements are defined by

$$\langle j'l'\tau'; J | V | j''l''\tau''; J\rangle = \int\int d\hat{R}' d\hat{r}'\, \mathcal{Y}_{j'l'\tau'}^{JM*}(\hat{r}', \hat{R}') \times V(\mathbf{r}, \hat{R}')\mathcal{Y}_{j''l''\tau''}^{JM}(\hat{r}', \hat{R}') , \tag{16}$$

and are independent of M.

The interaction potential between an asymmetric top and an atom may be written

$$V(\mathbf{r}, \hat{R}') = \sum_{\lambda=0}^{\infty} \sum_{\nu=-\lambda}^{\lambda} (4\pi/2\lambda+1)^{1/2} v_{\lambda\nu}(r) Y_{\lambda\nu}(\theta, \phi) , \tag{17}$$

where θ and ϕ are the angles that prescribe the orientation of the atom relative to the top. Since (θ, ϕ) are not the angles used previously and integration over angles is required by Eq. (16), the group representation property[24] is used to write $Y_{\lambda\nu}(\theta, \phi)$ as a function of $\hat{r}'$ and $\hat{R}'$. Hence the potential may be written

$$V(\mathbf{r}, \hat{R}') = \sum_{\lambda\nu\nu'} (4\pi/2\lambda+1)^{1/2} v_{\lambda\nu}(r) Y_{\lambda\nu'}(\hat{R}') D_{\nu'\nu}^{\lambda}(\hat{r}') . \tag{18}$$

Substituting Eqs. (3), (13), and (18) into Eq. (16) yields the following expression for the coupling matrix elements

$$\langle j'l'\tau';J|\,V\,|j''l''\tau'';J\rangle = (-)^{j'+j''-J}\sum_{k'=-j'}^{j'}\sum_{k''=-j''}^{j''} a^{j'}_{k',\tau'}a^{j''}_{k'',\tau''}(-)^{k''}\sum_{\lambda} v_{\lambda,k'-k''}(r)[(2j'+1)(2j''+1)(2l'+1)(2l''+1)]^{1/2}$$

$$\times\begin{pmatrix} l' & l'' & \lambda \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} j' & j'' & \lambda \\ k' & -k'' & k''-k'\end{pmatrix}\begin{Bmatrix} j' & l' & J \\ l'' & j'' & \lambda\end{Bmatrix} . \tag{19}$$

The $(:::)$ are 3-j symbols and $\{:::\}$ is a 6-j symbol.[25]

Symmetry considerations simplify evaluation of the coupling matrix elements. Conservation of parity requires the coupling matrix elements Eq. (19), to vanish unless

$$(-)^{j'+k'+s'+l'} = (-)^{j''+k''+s''+l''} . \tag{20}$$

(Recall from Sec. II that τ implies odd *or* even values of k and s to be 0 *or* 1.) Hermiticity of the potential results in

$$\langle j''l''\tau'';J|\,V\,|j'l'\tau';J\rangle = \langle j'l'\tau';J|\,V\,|j''l''\tau'';J\rangle . \tag{21}$$

The boundary condition on the radial function

$$u^J_{j'l'\tau',-j1\tau}(r) \sim \delta_{jj'}\delta_{ll'}\delta_{\tau\tau'}\exp[-i(k_{j\tau}r - l\pi/2)]$$

$$-\left(\frac{k_{j\tau}}{k_{j'\tau'}}\right)^{1/2} S^J_{j'l'\tau',-j1\tau}\exp[i(k_{j\tau}r - l\pi/2)] \tag{22}$$

defines the scattering matrix S^J. For the $j'\tau' - j\tau$ transition the integral cross section is given by

$$\sigma_{j'\tau',-j\tau} = \frac{\pi}{(2j+1)k^2_{j\tau}}\sum_{J=0}^{\infty}(2J+1)$$

$$\times\sum_{l=|J-j|}^{J+j}\sum_{l'=|J-j'|}^{J+j'}|\,T^J_{j'l'\tau',-j1\tau}\,|^2 , \tag{23}$$

where

$$T^J_{j'l'\tau',-j1\tau} = \delta_{jj'}\delta_{ll'}\delta_{\tau\tau'} - S^J_{j'l'\tau',-j1\tau} . \tag{24}$$

The cross section in Eq. (23) has been obtained by averaging over initial projections m_j and summing over final projections m'_j. Since the S matrix is unitary, the cross section for the reverse transition of a known one can be obtained from the reciprocity relation

$$\sigma_{j\tau,-j'\tau'} = [(2j+1)k^2_{j\tau}/(2j'+1)k^2_{j'\tau'}]\sigma_{j'\tau',-j\tau} . \tag{25}$$

IV. POTENTIAL ENERGY SURFACE

A previously computed *ab initio* interaction potential is used in the present study. The potential was constructed using a series of Hartree–Fock (HF) calculations[16] as a starting point which were subsequently improved upon by including effects of electron correlation via large scale (up to 38 000 configurations) configuration interaction (CI).[17]

To facilitate its use in the CC formulation of Sec. III, the potential is expanded in spherical harmonics with coefficients that are a function of r only [see Eq. (17)]. These coefficients are tabulated in Appendix B of Ref. 16 and fit to the form

$$v^{HF}_{\lambda\nu}(r) = \begin{cases} Ae^{-Br} - Cr^{-6} - Dr^{-2}, & r \le 10.5 \text{ a.u.} \\ 0, & r > 10.5 \text{ a.u.}\end{cases} \tag{26}$$

The constants A, B, C, and D are listed in Table I for each (λ, ν) pair.

TABLE I. Parameters for the HF interaction.[a,b]

λ	ν	A	B	C	D
0	0	3.034 (7)	1.845	−4.793 (6)	5.635 (7)
1	0	−2.483 (7)	1.751	1.226 (7)	−1.186 (8)
2	0	5.449 (7)	1.890	−6.558 (6)	7.320 (7)
2	2	8.094 (6)	1.735	−3.628 (6)	3.789 (7)
3	0	−1.056 (8)	2.586	−7.069 (5)	1.354 (6)
3	2	−1.546 (7)	1.736	8.259 (6)	−8.037 (7)
4	0	−3.534 (6)	1.535	9.527 (6)	−9.868 (7)
4	2	1.853 (7)	1.759	−6.595 (6)	6.644 (7)
4	4	1.891 (6)	1.774	−7.542 (5)	8.072 (6)
5	0	9.850 (6)	1.748	−3.935 (6)	3.771 (7)
5	2	−1.483 (7)	1.810	3.471 (6)	−3.309 (7)
5	4	−3.876 (6)	1.773	2.176 (6)	−2.133 (7)
6	0	−6.766 (6)	1.773	2.240 (6)	−2.139 (7)
6	2	9.097 (6)	1.867	−6.458 (5)	6.286 (6)
6	4	5.635 (6)	1.849	−1.443 (6)	1.405 (7)
6	6	1.054 (6)	2.084	−1.275 (5)	1.425 (6)
7	0	2.065 (6)	1.736	−9.935 (5)	9.736 (6)
7	2	−1.527 (6)	1.765	6.644 (5)	−6.362 (6)
7	4	−7.489 (6)	1.970	4.087 (5)	−4.048 (6)
7	6	−1.423 (6)	1.999	2.603 (5)	−2.759 (6)
8	0	6.528 (6)	2.340	−1.211 (5)	8.455 (5)
8	2	−2.540 (6)	2.123	−6.083 (3)	2.294 (5)
8	4	6.741 (6)	2.032	−1.058 (5)	1.096 (6)
8	6	2.284 (6)	2.072	−1.670 (5)	1.855 (6)
8	8	2.483 (6)	2.440	7.301 (4)	−6.220 (5)
9	0	−1.018 (6)	1.827	1.612 (5)	−1.453 (6)
9	2	1.458 (6)	1.900	−5.968 (5)	5.435 (5)
9	4	−3.530 (6)	2.011	9.729 (4)	−9.621 (5)
9	6	−3.149 (6)	2.154	7.576 (4)	−8.948 (5)
9	8	−1.829 (5)	1.749	9.982 (4)	−1.005 (6)
10	0	5.618 (5)	1.909	−2.721 (4)	1.752 (5)
10	2	−5.311 (5)	1.916	1.599 (4)	−1.309 (5)
10	4	1.374 (6)	2.003	−4.401 (4)	4.150 (5)
10	6	3.146 (6)	2.191	−2.969 (4)	4.099 (5)
10	8	2.936 (5)	1.818	−8.167 (4)	8.218 (5)
10	10	1.088 (6)	2.730	9.658 (3)	−8.540 (4)
11	0	1.532 (5)	1.681	−9.677 (4)	1.023 (6)
11	2	−2.037 (5)	1.763	7.733 (4)	−7.618 (5)
11	4	−2.004 (5)	1.950	1.693 (4)	−1.453 (5)
11	6	−2.502 (6)	2.206	1.243 (4)	−2.111 (5)
11	8	−4.106 (5)	1.881	7.275 (4)	−7.134 (5)
11	10	−1.562 (4)	1.691	1.133 (4)	−1.127 (5)
12	0	−3.089 (5)	1.730	1.869 (5)	−1.840 (6)
12	2	4.697 (5)	1.811	−9.500 (4)	9.246 (5)
12	4	−1.694 (5)	1.982	2.674 (3)	−5.278 (4)
12	6	−1.825 (6)	2.232	7.190 (2)	5.528 (4)
12	8	4.479 (5)	1.913	−5.518 (4)	5.421 (5)
12	10	2.446 (4)	1.734	−8.733 (3)	9.300 (4)
12	12	−2.358 (1)	1.273	3.639 (2)	−4.978 (3)

[a] Distance units are a.u. and energy units are °K. Values in parenthesis are powers of 10.
[b] See Eq. (26).

TABLE II. Parameters for the correlation interaction.[a,b]

θ	A	B	C
0°	−1.30529 (4)	0.80863	8.19754 (5)
90°	−5.58237 (4)	1.11606	2.08846 (5)
180°	−8.00165 (4)	1.01991	3.46152 (6)

[a]Distance units are a.u. and energy units are °K. Values in parenthesis are powers of 10.
[b]See Eq. (27).

In Eqs. (2)–(4) of Ref. (17), the correlation contributions $v_{\lambda\nu}^{\rm corr}(r)$ ($\lambda = 0, 1, 2$ and $\nu = 0$) are given in terms of $V(r, \theta)$ for $\theta = 0°$, 90°, and 180°. These radial functions have been fit to the form

$$V(r) = Ae^{-Br} - Cr^{-6} . \tag{27}$$

Values of A, B, and C for $\theta = 0°$, 90°, and 180° are listed in Table II.

The coefficients $v_{\lambda\nu}^{\rm HF}$ and $v_{\lambda\nu}^{\rm corr}$ are then combined to yield the $v_{\lambda\nu}(r)$ of Eq. (17) which fully defines the interaction potential.

V. SCATTERING CALCULATIONS

A. Description

Cross sections for rotational excitation of ortho H_2CO by collision with He were determined by integrating Eq. (14). In order to carry out the integration, it is necessary to specify the total energy of the system $E_{\rm tot}$ [see Eq. (11)], the number of internal H_2CO states, and the integration procedure. For the astrophysical application, Boltzmann averaged rate constants are required (see Sec. VI), and accordingly 12 values of $E_{\rm tot}$ in the range $20° \le E_{\rm tot} \le 95$ °K were chosen. (See either Table III or Table IV for a listing.) Since the sums on the right hand side of the CC equations (14) extend, in principle, over an infinite number of (j, τ, l) combinations, they must be truncated to obtain a computationally tractable problem. This is achieved by first choosing a basis of internal ortho H_2CO states (j, τ) and then selecting all values of orbital angular momentum l compatible with the triangle inequalities of angular momentum coupling for a given value of the total angular momentum J. For the present calculations, a basis set of 16 ortho H_2CO states with $1 \le j \le 5$ were chosen which results in a maximum of 62 coupled channels, i.e., (j, τ, l) combinations. For $E_{\rm tot} < 50$ °K, there are 4–8 H_2CO states energetically accessible in the asymptotic region. The CC equations were integrated using Gordon's method.[26]

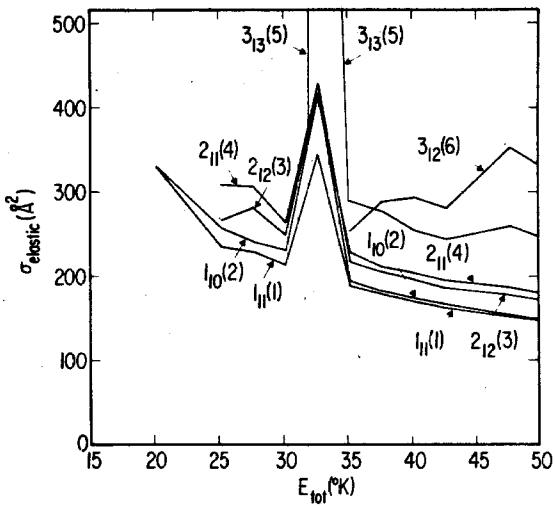

FIG. 2. Elastic cross sections. Energies at which cross sections were computed are listed in Table III.

B. Results

Elastic cross sections for the eight lowest ($j \le 4$) ortho H_2CO states are listed in Table III and displayed versus $E_{\rm tot}$ in Fig. 2. Cross sections for all excitation transitions among these states are given in Table IV. Selected inelastic cross sections are plotted in Fig. 3. De-excitation cross sections were obtained using the reciprocity relation in Eq. (25).

Resonances occur at approximately 20.2, 32.7, and 47.7 °K in many of the integral cross section versus $E_{\rm tot}$ curves. These energies are approximately equal to the internal energies of the $j = 2$, 3, and 4 doublets, respectively. A systematic study of this resonance structure was beyond the scope of the study.

VI. COOLING OF INTERSTELLAR H_2CO

In order to test the collisional pump as a mechanism for cooling of interstellar H_2CO, the rotational cross sections given in Sec. V are used to determine excitation temperatures. For simplicity we assume that the only processes of importance are dipole radiation and collisions. Higher moment transition probabilities are

TABLE III. Coupled channel elastic cross sections.[a]

	$E_{\rm tot}$(°K)										
State	20.1668	25.1668	27.6668	30.1668	32.6668	35.1668	37.6668	40.1668	42.6668	47.6668	70.1668	95.1668
1_{11}	331	235	229	213	345	189	179	170	163	152	115	93
1_{10}	331	257	241	231	418	194	182	174	167	154	115	93
2_{12}	···	267	282	249	430	217	205	197	186	178	122	96
2_{11}	···	308	306	263	414	228	211	204	195	187	124	97
3_{13}	···	···	···	···	1620	289	277	255	244	259	135	103
3_{12}	···	···	···	···	···	253	288	293	281	353	142	106
4_{13}	···	···	···	···	···	···	···	···	···	950	162	112
4_{12}	···	···	···	···	···	···	···	···	···	···	178	116

[a]Units are Å^2.

TABLE IV. Coupled channel inelastic cross sections.[a]

Transition	E_{tot}(°K) 20.1668	25.1668	27.6668	30.1668	32.6668	35.1668	37.6668	40.1668	42.6668	47.6668	70.1668	95.1668
$1_{11}\rightarrow 1_{10}$	66.0	25.6	17.8	15.1	45.5	12.3	11.5	11.1	10.1	9.5	7.6	6.6
$1_{11}\rightarrow 2_{12}$	···	22.7	23.3	23.3	37.6	20.2	18.1	17.1	16.7	16.1	10.5	8.5
$1_{11}\rightarrow 2_{11}$	···	12.2	11.8	13.9	17.1	11.2	9.5	8.9	8.0	7.7	5.7	5.2
$1_{11}\rightarrow 3_{13}$	···	···	···	···	4.8	4.1	5.4	6.3	6.4	8.0	5.4	4.6
$1_{11}\rightarrow 3_{12}$	···	···	···	···	···	0.3	0.6	0.8	1.2	1.6	0.9	1.3
$1_{11}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	3.0	3.5	3.8
$1_{11}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	0.9	1.2
$1_{10}\rightarrow 2_{12}$	···	13.4	13.8	15.4	33.1	11.5	9.9	9.7	9.2	8.5	6.3	5.4
$1_{10}\rightarrow 2_{11}$	···	14.2	13.3	16.0	34.9	14.3	12.4	11.6	10.3	8.9	8.4	7.8
$1_{10}\rightarrow 3_{13}$	···	···	···	···	2.5	7.6	8.6	7.6	7.2	7.0	4.7	3.4
$1_{10}\rightarrow 3_{12}$	···	···	···	···	···	1.6	2.4	2.6	3.7	4.7	4.5	4.3
$1_{10}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	3.0	2.5	2.2
$1_{10}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	0.6	0.7
$2_{12}\rightarrow 2_{11}$	···	24.8	19.4	19.9	92.4	13.1	10.4	8.4	7.1	5.5	3.5	2.8
$2_{12}\rightarrow 3_{13}$	···	···	···	···	10.8	11.9	13.3	13.3	12.9	20.0	11.6	11.1
$2_{12}\rightarrow 3_{12}$	···	···	···	···	···	2.1	3.3	3.7	3.7	9.5	3.4	3.1
$2_{12}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	4.2	3.0	3.3
$2_{12}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	1.1	1.3
$2_{11}\rightarrow 3_{13}$	···	···	···	···	7.6	7.1	7.9	6.8	7.3	12.3	3.7	2.8
$2_{11}\rightarrow 3_{12}$	···	···	···	···	···	8.2	11.5	12.1	10.4	20.2	9.5	8.2
$2_{11}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	4.2	3.9	3.4
$2_{11}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	3.3	3.6
$3_{13}\rightarrow 3_{12}$	···	···	···	···	···	9.6	10.2	8.8	9.2	25.0	2.8	2.1
$3_{13}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	14.1	11.9	10.7
$3_{13}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	2.4	2.4
$3_{12}\rightarrow 4_{14}$	···	···	···	···	···	···	···	···	···	12.7	2.6	1.9
$3_{12}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	10.0	9.6
$4_{14}\rightarrow 4_{13}$	···	···	···	···	···	···	···	···	···	···	2.7	1.8

[a]Units are Å^2.

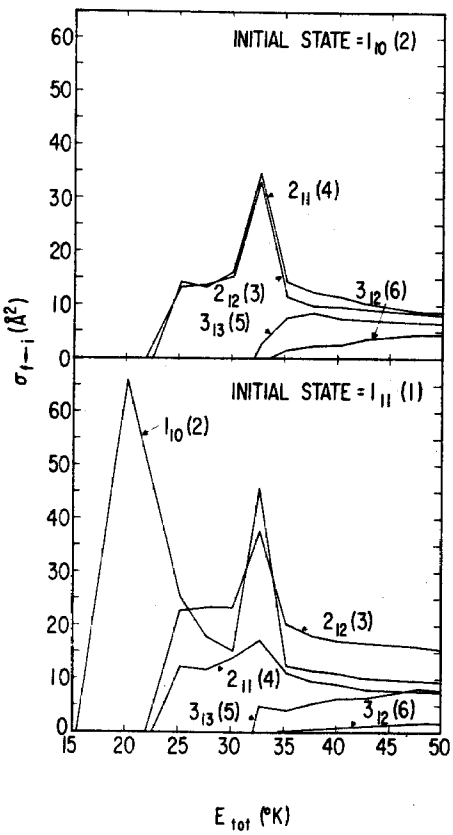

FIG. 3. Inelastic cross sections for initial states 1_{11} and 1_{10}. Energies at which cross sections were computed are listed in Table IV.

several orders of magnitude smaller than dipolar ones and hence assumed negligible here.[27] It is also assumed that the interstellar medium is rare enough to neglect radiative trapping.

Astrophysical observations indicate that the 6 cm ($j=1$) and 2 cm ($j=2$) doublets of ortho H_2CO are cooled, i.e., the excitation temperatures T_{exc} between states 1 and 2 (see Fig. 1) and between states 3 and 4 are less than either the isotropic background temperature ($T_{iso} \simeq 2.7$ °K) or the kinetic temperature ($10 \leq T_k \leq 20$ °K). The excitation temperature is defined by assuming a Boltzmann distribution for the populations of two internal states, viz.,

$$n_i/n_j = (g_i/g_j)\exp[-(E_i - E_j)/k_B T_{exc}], \tag{28}$$

where n_i is the population of the ith internal state, g_i is the degeneracy of the ith internal state, E_i is the energy of the ith internal state, and k_B is the Boltzmann's constant. Thus if the populations of two states are known, then the excitation temperature characterizing them can be determined.

The populations are determined by solving the equations of statistical equilibrium,[28]

$$\frac{dn_i}{dt} = \sum_{j\neq i}\{A_{ji} + B_{ji}\rho(\nu_{ij}) + [\mathrm{He}]k_{ji}\}n_j - \left\{\sum_{j\neq i} A_{ij} + B_{ij}\rho(\nu_{ij}) + [\mathrm{He}]k_{ij}\right\}n_i = 0 \tag{29}$$

TABLE V. Rate constants[a] at $T_k = 15\,^\circ$K.

Initial state	Final state							
	1_{11}	1_{10}	2_{12}	2_{11}	3_{13}	3_{12}	4_{14}	4_{13}
1_{11}	•••	5.5	5.0	2.5	1.3	0.2	0.4	0.1
1_{10}	5.6	•••	3.1	3.4	1.3	0.8	0.3	0.0
2_{12}	4.7	2.8	•••	3.9	3.8	1.3	0.6	0.1
2_{11}	2.5	3.3	4.1	•••	2.0	3.4	0.6	0.3
3_{13}	1.7	1.7	5.3	2.7	•••	3.4	2.8	0.3
3_{12}	0.3	1.1	2.1	4.9	3.8	•••	1.5	1.4
4_{14}	1.0	0.8	1.6	1.7	5.4	2.6	•••	0.5
4_{13}	0.2	0.1	0.3	0.9	0.7	2.9	0.6	•••

[a]In units of 10^{-11} cm^3/molecule-sec.

where A_{ij} is the Einstein coefficient for spontaneous dipole emission from state i to state j ($E_i > E_j$), B_{ij} is the Einstein coefficient for induced dipole emission and absorption, $\rho(\nu_{ij})$ is the energy distribution of radiation at the isotropic background temperature (2.7 °K), $\nu_{ij} = |E_i - E_j|/h$ and [He] is the helium concentration.[27] Here k_{ij} is the collisional rate constant for transition from state i to state j obtained by a Boltzmann average of the inelastic cross sections (as determined in Sec. V) as follows (see Table V):

$$k_{ij}(T_k) = \left(\frac{8}{\pi\mu(k_B T_k)^3}\right)^{1/2} \int_0^\infty E\sigma_{ji}(E)\, e^{-E/k_B T_k}\, dE\,, \qquad (30)$$

where $E = E_{\rm tot} - E_i$ is the relative translational energy.

Assuming a kinetic temperature and a helium concentration, the system of equations defined by Eq. (29) is solved for the ratio of populations n_i/n_j. Excitation temperatures are then calculated using Eq. (28). In the limit [He] $\to 0$, radiative processes dominate and all of the excitation temperatures reduce to $T_{\rm iso}$. As [He] $\to \infty$ the collisional processes become dominant and all $T_{\rm exc} \to T_k$. At helium concentrations between these limits $T_{\rm exc}$ may lie lower than both $T_{\rm iso}$ and T_k.

Figure 4 displays cooling curves ($T_{\rm exc}$ vs [He]) at T_k = 5, 10, 15, and 20 °K. Cooling of both the 6 cm (T_{12}) and 2 cm (T_{34}) doublets is seen to occur at helium concentrations between 10^2 and 10^5 cm^{-3} for kinetic temperatures between 10 and 20 °K but not for 5 °K. The two remaining curves, T_{13} and T_{24}, are excitation temperatures for dipole allowed transitions.

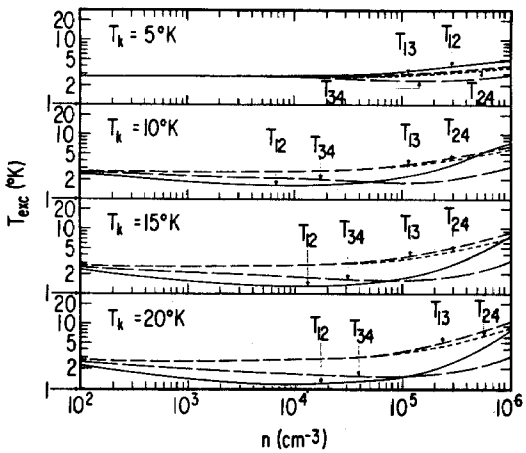

FIG. 4. Excitation temperatures as a function of He density at selected kinetic temperatures.

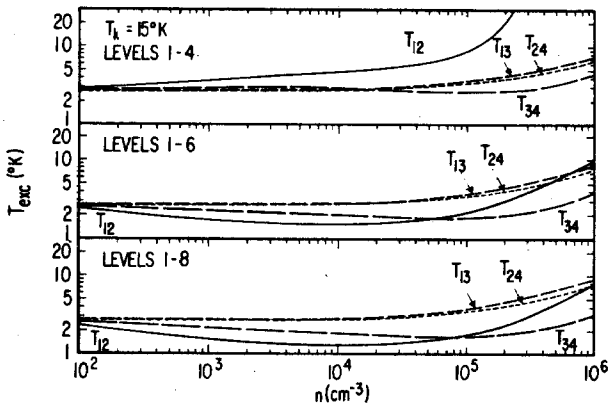

FIG. 5. Excitation temperatures as a function of He density with various numbers of internal states included in the equations of statistical equilibrium, see Eq. (29).

Having established that the 6 and 2 cm doublets of H_2CO are cooled by a collisional pump, the question of the relative importance of the various transitions remains to be fully elucidated. By varying the number of states used in the equations of statistical equilibrium [limit of summation in Eq. (29)], the effect of the different j doublets on the cooling can be assessed (see Fig. 5). Neglecting the $j = 4$ levels caused less than 0.2 °K changes in the effective temperatures for He concentrations at which cooling occurs. Omission of the $j = 3$ levels, however, resulted in *no* cooling of H_2CO. At low He concentrations ($\lesssim 10^5$ cm^{-3}) radiative contributions are found to dominate collisional dipole allowed transitions, so that rate constants k_{12}, k_{13}, k_{24}, k_{34}, k_{35}, k_{46}, and k_{56} are of minor importance. Ratios of dipole forbidden transitions, e.g., k_{25}/k_{16}, are the indicators of cooling. The large ratio of $k_{25}/k_{16} \approx 6$ (Table V) implies that transitions from the $j = 1$ to the $j = 3$ doublets are the primary components of the cooling mechanism.

For collisions of the isotopic homologue $H_2{}^{13}CO$, the Born–Oppenheimer interaction potential is the same as before and all differences are contained in the dynamical treatment. They involve small changes in the center of mass of H_2CO, the reduced mass of the total system and the energy level spacing. These differences are expected to have little effect on the scattering cross sections. In agreement with observations, these calculations imply that the $j = 1$ doublet of $H_2{}^{13}CO$ would also be cooled.

VII. SUMMARY

The quantum mechanical theory of scattering of a rigid rotator by a structureless projectile was extended to treat collisions of a rigid asymmetric top and applied to the scattering of ortho H_2CO by He at interstellar temperatures. Using a previously determined *ab initio* configuration interaction potential energy surface, cross sections for rotational energy transfer were computed by the coupled-channel method and averaged over a Boltzmann distribution to obtain collision rates needed

to test the collisional pumping model for cooling of the 6 and 2 cm doublets of ortho H_2CO. The present study shows that these doublets are cooled by collisions with He. (It is anticipated that collisions with H_2 will show the same behavior.) Thus the calculations described above confirm the Townes–Cheung model and, in addition, unambiguously show that cooling proceeds through a three-doublet mechanism rather than a two-doublet one.

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