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SEMICLASSICAL TREATMENT OF ATOM - ASYMMETRIC ROTOR COLLISIONS; ROTATIONAL EXCITATION OF FORMALDEHYDE AT LOW ENERGIES*

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ABSTRACT

The formalism necessary for the application of "classical S-matrix" theory to collisions of an atom with a rigid asymmetric rotor is derived. This is applied to rotational excitation of formaldehyde by H_2 (taken to be spherically symmetric) at energies from 10°K to 15°K. Classical Monte Carlo trajectory calculations were also carried out for the same system in the energy range 10°K to 40°K. The results support the proposal of Townes and Cheung that a collisional mechanism is responsible for the $1_{11} \rightarrow 1_{10}$ anomalous absorption of formaldehyde in cool interstellar dust clouds.

I. INTRODUCTION.

The $1_{11} \rightarrow 1_{10}$ transition of formaldehyde is seen in absorption against the 2.7°K cosmic background radiation in cool interstellar dust clouds, indicating that the lower state (1_{11}) has a population greater than would be expected if the system were in equilibrium with the background radiation.[1,2] Townes and Cheung[3] have noted that since the 2_{12} state spontaneously decays (via a dipole-allowed transition) to the 1_{11} state, while the 2_{11} state spontaneously decays to the 1_{10} state, collisional excitation which favors the 2_{12} over the 2_{11} state could produce the observed "cooling" (i.e., enhancement of the population of the 1_{11} state). They further argue[3] that since the 2_{12} state corresponds to the rotational angular momentum being predominantly about the axis perpendicular to the plane of the molecule, collisional excitation of formaldehyde from a $j = 1$ state to a $j = 2$ state should indeed be preferentially to the 2_{12} state. The results of the calculations presented in this paper do show the cross sections for the $1_{10} \rightarrow 2_{12}$ and $1_{11} \rightarrow 2_{12}$ excitations to be larger than those for the $1_{10} \rightarrow 2_{11}$ and $1_{11} \rightarrow 2_{11}$ excitations, thus lending support to the Townes-Cheung mechanism.

In the present calculation the collision partner of formaldehyde is taken to be H_2, which is assumed to be spherically symmetric. A model potential is used which, although probably not an accurate representation of the actual potential, should give the essential features of the collision process correctly. All internal degrees of freedom of H_2 and all vibrational degrees of freedom of formaldehyde are ignored.

The cross sections for the rotational excitation transitions have been obtained by Monte Carlo trajectory methods[4] and by application of "classical S-matrix" theory,[5] a semiclassical approach that uses numerically computed classical trajectories in combination with essential quantum mechanical features. A number of applications[5-7] to atom-diatom collision processes have shown that this semiclassical theory is often an accurate description of the quantum effects in molecular collisions; the present work is the first application of it to collisions involving a polyatomic molecule. The classical Monte Carlo calculations are much simpler to carry out and were done for the energy range 10-40°K. The semiclassical calculations were performed at four energies in the range 10-15°K to provide a check on the reliability of the purely classical results. Apart from an interference structure in the semiclassical results, the two approaches are in reasonable agreement.

The paper is organized as follows: Section II discusses first how an isolated asymmetric rotor is described semiclassically. Classical S-matrix theory for atom-asymmetric rotor collisions is summarized in Section III, along with specific aspects of the present applications; the way in which Monte Carlo trajectory calculations were carried out is also described here and in Appendix C. The results of the calculations are presented and discussed in Section IV.

II. SEMICLASSICAL DESCRIPTION OF THE ISOLATED ASYMMETRIC ROTOR.

In order to apply classical S-matrix theory[5] to a bimolecular collision process it is first necessary to describe the internal quantum states (i.e., rotational-vibrational states) of the isolated collision partners. This section, therefore, considers the semiclassical description of an isolated asymmetric rotor.

Consider an asymmetric rotor[8] with principal moments of inertia I_x, I_y, I_z such that $I_z \geq I_y \geq I_x$. Letting $A = \frac{1}{2I_x}$, $B = \frac{1}{2I_y}$, $C = \frac{1}{2I_z}$; the asymmetry parameter κ is defined by

$$\kappa = \frac{2B - A - C}{A - C} \tag{2.1}$$

For a prolate symmetric top $I_y = I_z$ and $\kappa = -1$ while for a oblate symmetric top $I_x = I_y$ and $\kappa = +1$.

The rigid asymmetric rotor has three degrees of freedom, and its classical Hamiltonian can be written as

$$H(j,m,k;\ q_j,q_m,a_k) = B(j^2-k^2)\cos^2 q_k + A(j^2-k^2)\sin^2 q_k + Ck^2 \tag{2.2}$$

This gives the Hamiltonian in terms of the action-angle variables of the system: j is the magnitude of the rotational angular momentum, m is its component along a space-fixed z axis, and k is its component along a body-fixed z axis. The q's are the angle variables conjugate to the momenta j,k, and m. In the oblate symmetric rotor limit, B = A, and the Hamiltonian becomes

$$H(j,m,k;\ q_j,q_m,q_k) = B(j^2-k^2) - (B-C)\,k^2 \tag{2.3a}$$

In the prolate symmetric rotor limit (B = C) one needs to define k' to be the projection of $\vec{j}$ along the body fixed x axis, and the Hamiltonian then becomes

$$H(j,m,k';\ q_j,q_m,q_{k'}) = B(j^2-k'^2) + (A - B)\ k'^2 \quad . \tag{2.3b}$$

Since (2.2) has no dependence on q_m or q_j, it can readily be seen that j and m are conserved. Likewise for a symmetric top k (or k') is also conserved.

The traditional way of quantizing the asymmetric rotor semiclassically[9] is to realize that it is essentially a system with only one degree of freedom, with j appearing in the Hamiltonian simply as a parameter; i.e., the one-dimensional Hamiltonian is

$$H_j(k,q_k) = (j^2-k^2)\ (A \sin^2 q_k + B \cos^2 q_k) + C\ k^2 \quad .$$

One then applies the Bohr-Sommerfeld quantum condition to this one dimensional system in order to quantize the k-degree of freedom:

$$2\pi\hbar(n + \tfrac{1}{2}) = \oint dq_k\ k(q_k,j,E) \tag{2.4}$$

where $k(q_k,j,E)$ is determined from the Hamiltonian by conservation of energy:

$$k(q_k,j,E) = \pm \left[\frac{E - j^2(A \sin^2 q_k + B \cos^2 q_k)}{C - A \sin^2 q_k - B \cos^2 q_k}\right]^{\frac{1}{2}} \tag{2.5}$$

Equation (2.4) can now in principle be inverted to give $E(j,n)$. This procedure, however, gives relatively poor results for the lowest quantum states which are our present concern. It would be desirable, therefore, to be able to use the correct quantum values for the energy levels within an internally consistent semiclassical framework.

For this purpose we define a new momentum variable η by

$$\eta^2 = (1 + \kappa)\, j_z^{\,2} - (1 - \kappa)\, j_x^{\,2} \tag{2.6}$$

where j_x and j_z are the components of $\vec{j}$ along the corresponding body-fixed axes. It may be noted that in the oblate limit $(\kappa = +1)$ $\eta^2 = 2\,k^2$ and in the prolate limit $(\kappa = -1)$ $\eta^2 = -2\,k'^2$. The classical Hamiltonian in terms of this new variable is given by

$$H(j,\eta;\, q_j, q_\eta) = Bj^2 - \frac{(A - C)}{2}\, \eta^2 \tag{2.7a}$$

so that η^2 is a constant of the motion. If one lets $j^2 = \hbar^2\, j(j + 1)$, $\nu^2 = \frac{\eta^2}{\hbar^2}$, $a = \hbar^2 A$ etc., then (2.7a) becomes

$$H = bj(j + 1) - \frac{(a - c)\nu^2}{2} \tag{2.7b}$$

so that ν is related to the quantum mechanical quantity $E(\kappa)$ by[8]

$$E(\kappa) = \kappa j(j + 1) - \nu^2 \quad . \tag{2.8}$$

The rotational state of the asymmetric rotor can now be described within the semiclassical framework by specifying the quantum number j and the quantity ν (determined from tabulated values of E (κ)). Appendix A carries out the canonical transformations necessary to replace k by η.

III. SEMICLASSICAL THEORY OF ATOM-ASYMMETRIC ROTOR COLLISIONS; METHODOLOGY

The cross section for the inelastic process

$$CH_2O\ (j_1,\nu_1) + H_2 \rightarrow CH_2O\ (j_2,\nu_2) + H_2$$

is given by

$$\sigma_{j_2\nu_2\leftarrow j_1\nu_1}(E) = \frac{\pi\hbar^2}{(2\mu E)\ (2j_1 + 1)} \sum_{J=0}^{\infty} (2\ J + 1) \sum_{\ell_1,\ell_2} |S^J_{\ell_2 j_2\nu_2,\ell_1 j_1\nu_1}|^2 \qquad (3.1)$$

where ℓ is the orbital angular momentum quantum number for relative translation of the collision partners, j and ν are the quantities that define the rotational state of the isolated formaldehyde as in equation (2.7b), J is the total angular momentum quantum number, rotational (j) plus orbital (ℓ), of the composite system, E is the initial translational energy, and μ is the reduced mass of the collision partners. The reader will recognize that (3.1) is identical in form to the expression for rotational-vibrational excitation in the atom-diatom collision system,[10] except that here ν is related to the components of j about body fixed axes rather than being a vibrational quantum number. The sums over ℓ_1 and ℓ_2 in (3.1) result from an average and a sum over the initial and final m states of the rotor, respectively.

The semiclassical approximation to the S-matrix elements in (3.1) is constructed according to the general prescription that has been given.[5,10] Again, the expression is of the same form as that for the atom-diatom rotational-vibrational system:[10,6d]

$$S^{J}_{\ell_2 j_2 \nu_2, \ell_1 j_1 \nu_1}(E) = \sum \left[(-2\pi\ i\ \hbar)^3 \frac{\partial(\ell_2, j_2, \nu_2)}{\partial(q_{\ell_1}, q_{j_1}, q_{\nu_1})} \right]^{-\frac{1}{2}} \tag{3.2}$$

$$\exp\ [\ i\ \phi\ (\ell_2 j_2 \nu_2, \ell_1 j_1 \nu_1)/\hbar] \quad ,$$

where the sum indicates a sum of such terms for all trajectories which obey the correct initial and final boundary conditions; see ref. 5 and 10 for more details.

In order to use equations (3.1) and (3.2) it is necessary that J^2 be quantized everywhere and that j^2, ℓ^2, and ν^2 be quantized in the initial and final asymptotic regions. J^2 and ℓ^2 are quantized by the usual Langer prescription

$$\begin{aligned} \ell^2 &\rightarrow \hbar^2\ (\ell + \tfrac{1}{2})^2 \\ J^2 &\rightarrow \hbar^2\ (J + \tfrac{1}{2})^2 \quad , \end{aligned} \tag{3.3}$$

ν^2 is "quantized" by setting it equal to the value determined from Eq. (2.8) by j and the quantum value of E(κ). The quantum mechanical quantization of j^2 (i.e., $j^2 \rightarrow \hbar^2 j(j+1)$) was retained because it was felt that this would be more accurate for treating the low rotational levels which were of interest in this calculation.

The numerically integrated classical trajectories needed to evaluate Eq. (3.2) may be computed in any convenient set of canonical variables as long as the proper transformation to the $\ell, j, \nu, q_\ell, q_j, q_\nu$ set is performed in the initial and final asymptotic regions. Formaldehyde is almost a prolate symmetric top ($\kappa = -0.9610644$ for the adopted geometry) so that the component of angular momentum along the CO bond axis of isolated formaldehyde is almost conserved.[11] Since the relationship between k and η is also not very tractable (see Appendix A), it was decided to compute the trajectories[12] in the $\ell, j, k, q_\ell, q_j, q_k$ set of canonical coordinates. Appendix B gives the canonical transformations and necessary relations for this coordinate set.

The classical Hamiltonian is given in this set of canonical variables by

$$H(p_R, \ell, j, k; R, q_\ell, q_j, q_k) = \frac{p_R^{\,2}}{2\mu} + \frac{\ell^2}{2\mu R^2} + j^2 \, [C \sin^2 q_k + B \cos^2 q_k]$$

$$+ k^2 \, (A - B \cos^2 q_k - C \sin^2 q_k) + V \, (R, \gamma, \zeta) \qquad (3.4)$$

where R is the distance between the centers of mass of the collision partners and μ is the reduced mass for the relative motion of the centers of mass (i.e., $\mu = \dfrac{m_{CH_2O} \, m_{H_2}}{m_{H_2} + m_{CH_2O}}$). The potential energy depends on only the three parameters (R, γ, ζ), where γ is the angle between $\vec{R}$ and the body-fixed z axis of formaldehyde, and ζ is the angle between $\vec{R}$ and the corresponding x axis.

A model potential of the form

$$V = \sum_{i=1}^{4} F_i \exp \, [-R_i^{\,2}/S_i] \qquad (3.5)$$

was adopted for the hydrogen molecule-formaldehyde interaction. This type of potential was used in order to make the results comparable with quantum mechanical calculations[2] which were in progress at the time this work was begun. The sum is over the four atoms making up the formaldehyde and R_i^2 is the square of the distance between the ith atom of formaldehyde and the H_2 center of mass. Table I lists the values of the parameters that were chosen for this work. The S_i values were chosen so that the "sizes" of the atoms for the energy range considered would be comparable to the usual Van der Waals radii of these elements in organic compounds.

This model potential is admittedly quite crude in that it neglects the long range attractive forces and that the short range repulsion is not steep enough. However, the quantity of interest for the astrophysical problem is the relative size of two cross sections, so that the detailed form of the potential beyond that which determines the effective sizes of the atoms may not significantly affect the result. The presumed effect of an attractive part of the potential would be to give the collision partner a higher kinetic energy when it hits the repulsive wall. It would be more important in grazing collisions, but at the kinetic energies considered it is probable that these collisions would not be able to effect the necessary energy transfer. Consequently, it is believed that the major effect of the neglected attractive well on the inelastic cross sections would be to shift the results in energy without dramatically affecting their shape.

The structure of formaldehyde given in ref. 8 was adopted for this work since it is the same as that used in ref. 2 and 3. The values given[8] for the rotational constants are A_o = 282,106 Mc; B_o = 38,834 Mc; and C_o = 34,004 Mc which correspond to an asymmetry parameter κ of -0.9610644. The adopted structure and the coordinate system used are shown in Figure 1. The values of the structural parameters with respect to the center of mass as shown in Figure 1b are then: $r_o = 0.9943\ a_o$, $r_c = 1.2925\ a_o$, $r_H = 2.9948\ a_o$, $\delta = 37.29°$. The energies and values of ν for all the $j = 1$ and $j = 2$ rotational states of formaldehyde are given in Table II. The distances required in Eq. (3.5) are now given in terms of the structural parameters and the potential parameters (R,γ,ζ) by

$$\begin{aligned}
R_o^{\,2} &= R^2 + r_o^{\,2} - 2\,R\,r_o\cos\gamma \\
R_c^{\,2} &= R^2 + r_c^{\,2} + 2\,R\,r_c\cos\gamma \\
R_{H_1}^2 &= R^2 + r_H^{\,2} + 2\,R\,r_H\,(\sin\delta\cos\zeta - \cos\gamma\cos\delta) \\
R_{H_2}^2 &= R^2 + r_H^{\,2} - 2\,R\,r_H\,(\sin\delta\cos\zeta + \cos\gamma\cos\delta)
\end{aligned} \tag{3.6}$$

Even at the low collision energies employed the excitation of the $j = 1$ states to $j = 2$ states is a "classically allowed"[13] process, i.e., there are real-valued classical trajectories which lead to these transitions. (There will also be some contribution from complex-valued classical trajectories, but this has been ignored in the present work.) In general there are a number of different classical trajectories (up to 8 in the present application) which contribute to each specific S-matrix element; because of the small difference in the classical actions along such trajectories it is important <u>not</u> to use the "primitive" semiclassical expression, Eq. (3.2), but rather the appropriate uniform asymptotic expression.[6c,6d,14] The semiclassical results discussed in the following section have all been "uniformized" in this way.

For the Monte Carlo trajectory calculations it was decided to modify the standard procedures[4] somewhat because only a few values of J, ℓ_1, and ℓ_2 contribute to the sums in Eq. (3.1) at these low collision energies. Proceeding along the lines of ref. 6c, therefore, J and ℓ_1 were retained as integers and the Monte Carlo procedure used to calculate the square modulus of S-matrix elements individually. Appendix C gives the details of this as it pertains to the atom-asymmetric rotor collision system.

IV. RESULTS AND DISCUSSION.

The cross sections for the rotational excitation of the 1_{11} and 1_{10} states to the 2_{12} and 2_{11} states of formaldehyde are shown in Figure 2; the solid line is the result of the Monte Carlo classical trajectory calculation, and the points are the semiclassical values at energies of 10, 11, 12, and 15°K. The semiclassical results show a strong interference structure which is not quenched by the sums in Eq. (3.1) because so few terms contribute. As expected,[15] the purely classical results do not reproduce this structure but appear to give the average result reasonably well. Since these cross sections would be averaged over a smooth distribution of translational energies in computing rate constants, the interference structure would not likely be important; if this is the case, then the classical Monte Carlo results would be sufficient. This is quite encouraging, of course, for the classical Monte Carlo trajectory calculations are considerably easier to carry out than the semiclassical ones.

Figure 3a shows the classical Monte Carlo results for the $1_{11} \rightarrow 1_{10}$ cross section as a function of collision energy E. Since microscopic reversibility implies that

$$\sigma(1_{11} \leftarrow 1_{10}) = \frac{E}{E - \Delta\varepsilon}\ \sigma(1_{10} \leftarrow 1_{11}) \quad , \qquad (4.1)$$

where $\Delta\varepsilon$ is the splitting of the 1_{11} and 1_{10} levels, $\Delta\varepsilon = 0.23182°K$, the cross sections for the $1_{10} \rightarrow 1_{11}$ and $1_{11} \rightarrow 1_{10}$ transitions are essentially equal at the energies E considered.

Although a number of additional complications[16] must be taken into account in a complete analysis of the "anomalous" absorption of formaldehyde, the following treatment may be of interest. If the rate of the dipole-allowed spontaneous decay of the $j = 2$ states to the $j = 1$ states (i.e., $2_{12} \rightarrow 1_{11}$ and $2_{11} \rightarrow 1_{10}$) were infinitely fast compared to inelastic collision rates, and if the radiative rates between the 1_{10} and 1_{11} states were neglibly slow, then simple considerations[3] imply that the steady-state ratio R of population of the 1_{11} state to that of the 1_{10} state would be

$$R = [\sigma(1_{11} \leftarrow 1_{10}) + \sigma(2_{12} \leftarrow 1_{10})] \div [\sigma(1_{10} \leftarrow 1_{11}) + \sigma(2_{11} \leftarrow 1_{11})] \quad . \tag{4.2}$$

This quantity is shown as a function of collision energy in Figure 3b, the cross sections being the Monte Carlo trajectory results from Figures 2 and 3a. The temperature T relating the 1_{11} and 1_{10} levels is defined by

$$R \equiv \exp(\Delta\varepsilon/kT) \quad ; \tag{4.3}$$

R = 1.1 and 1.2, for example, implies a temperature T = 2.4°K and 1.3°K, respectively. With the cross sections replaced by ones suitably averaged over translational energy--which would effectively smooth out the R versus E relation in Figure 3b--this is in good qualitative agreement with the observed[1] population ratio corresponding to $T \sim 1.8$°K.

In summary, therefore, the results of our calculations do show that rotational excitation of formaldehyde from the 1_{11} and

1_{10} levels to the 2_{12} level is favored over that to the 2_{11} level, in accord with Townes and Cheung,[3] and the magnitude of the effect is consistent with this being the cooling mechanism responsible for the anomalous absorption of formaldehyde in interstellar dust clouds. The weakest aspect of the present calculations is probably the interaction potential, although it would also be useful to have completely quantum mechanical scattering calculations to check the reliability of the classical and semiclassical results.

APPENDIX A. SEMICLASSICAL TREATMENT OF THE ASYMMETRIC ROTOR

Let x,y,z be the principal axes of the molecule with $I_z \geq I_y \geq I_x$. For a prolate symmetric top $I_y = I_z$ and for an oblate symmetric top $I_x = I_y$. The classical Hamiltonian is

$$H = \frac{I_x\omega_x^2}{2} + \frac{I_y\omega_y^2}{2} + \frac{I_z\omega_z^2}{2} \tag{A.1}$$

where the ω's are the angular velocities about the appropriate axes. Now introducing the Euler angles θ,ϕ,ψ of the body[17] we have

$$\begin{aligned}
\omega_x &= \dot{\phi} \sin\theta \sin\psi + \dot{\theta} \cos\psi \\
\omega_y &= \dot{\phi} \sin\theta \cos\psi - \dot{\theta} \sin\psi \\
\omega_z &= \dot{\phi} \cos\theta + \dot{\psi}
\end{aligned} \tag{A.2}$$

so that

$$\begin{aligned}
p_\phi &= I_x\omega_x \sin\theta \sin\psi + I_y\omega_y \sin\theta \cos\psi + I_z\omega_z \cos\theta \\
p_\theta &= I_x\omega_x \cos\psi - I_y\omega_y \sin\psi \\
p_\psi &= I_z\omega_z
\end{aligned} \tag{A.3}$$

are the momenta conjugate to the Euler angles. Inverting the momentum relations gives

$$j_x = I_x\omega_x = \frac{p_\phi \sin\psi}{\sin\theta} + p_\theta \cos\psi - \frac{p_\psi \cos\theta \sin\psi}{\sin\theta}$$

$$j_y = \frac{p_\phi \cos\psi}{\sin\theta} - p_\theta \sin\psi - p_\psi \frac{\cos\theta \cos\psi}{\sin\theta} \tag{A.4}$$

$$j_z = p_z$$

for the body fixed components of the rotational angular momentum. The Hamiltonian is now

$$H(\theta,\phi,\psi,p_\theta,p_\phi,p_\psi) = A\left[\frac{p_\theta \sin\psi}{\sin\theta} + p_\theta \cos\psi - \frac{p_\psi \cos\theta \sin\psi}{\sin\theta}\right]^2$$

$$+ B\left[\frac{p_\phi \cos\psi}{\sin\theta} - p_\theta \sin\psi - \frac{p_\psi \cos\theta \cos\psi}{\sin\theta}\right]^2 + Cp_\psi^2 \tag{A.5}$$

where $A = \frac{1}{2I_x}$, $B = \frac{1}{2I_y}$, $C = \frac{1}{2I_z}$ and the square of the magnitude of the angular momentum is

$$\vec{j}^2 = j_x^{\ 2} + j_y^{\ 2} + j_z^{\ 2} = p_\theta^{\ 2} + \frac{1}{\sin^2\theta}\left[p_\phi^{\ 2} + p_\psi^{\ 2} - 2p_\phi\, p_\psi \cos\theta\right] \tag{A.6}$$

The asymmetry parameter κ is defined by $\kappa = \frac{2B - A - C}{A - C}$ so that $\kappa = +1$ for an oblate symmetric top and $\kappa = -1$ for a prolate symmetric top. The quantity $E(\kappa)$ which can be calculated quantum mechanically is defined by

$$2\,E = (a + c)\, j\,(j + 1) + (a - c)\, E\,(\kappa) \tag{A.7}$$

where $a = \hbar^2 A$ etc.

We now eliminate p_θ in favor of j, the magnitude of the rotational angular momentum by a canonical transformation using an F_2 generator.[16]

This generator is

$$F_2\ (\theta,\phi,\psi,j,m,k) = \phi\ m + \psi\ k + j\ \cos^{-1}\left[\frac{j^2\cos\theta - mk}{\sqrt{(j^2-k^2)(j^2-m^2)}}\right]$$

$$- m\ \cos^{-1}\left[\frac{m\cos\theta - k}{\sin\theta\sqrt{j^2-m^2}}\right] - k\ \cos^{-1}\left[\frac{k\cos\theta - m}{\sin\theta\sqrt{j^2-k^2}}\right] \tag{A.8}$$

where $m = p_\phi$ is the component of $\vec{j}$ along the space-fixed z axis and $k = p_\psi$ is the component of $\vec{j}$ along the body-fixed z axis. Now the new coordinates (which are the coordinates canonically conjugate to j,m,k) and the transformed Hamiltonian are

$$q_j = \cos^{-1}\left[\frac{j^2\cos\theta - mk}{\sqrt{j^2-k^2}\sqrt{j^2-m^2}}\right] \tag{A.9}$$

$$q_m = \phi - \cos^{-1}\left[\frac{m\cos\theta - k}{\sin\theta\sqrt{j^2-m^2}}\right]$$

$$q_k = \psi - \cos^{-1}\left[\frac{k\cos\theta - m}{\sin\theta\sqrt{j^2-k^2}}\right]$$

$$H(j,k,m,q_j,q_k,q_m) = j^2\ [A\ \sin^2 q_k + B\ \cos^2 q_k]$$

$$+ k^2\ [C - A\ \sin^2 q_k - B\ \cos^2 q_k] \tag{A.10}$$

Since q_k is the only coordinate present in the Hamiltonian, it is now obvious that j and m are conserved whereas k is not (unless A = B).

It can now be seen from (A.10) that we have an effectively one-dimensional problem and that the semiclassical energy levels might be calculated by applying the Bohr-Sommerfeld quantization rules to the k, q_k system (with j as a constant parameter). This would give

$$2\pi\hbar\left(n+\frac{1}{2}\right)=\int_0^{2\pi} dq_k \left[\frac{E - j^2(A\sin^2 q_k + B\cos^2 q_k)}{C - A\sin^2 q_k - B\cos^2 q_k}\right]^{\frac{1}{2}} \tag{A.11}$$

with $j^2 = \hbar^2 j\ (j + 1)$. In the limit A = B (κ = +1) we would get the correct quantum result that $n = k_+$ but in the limit B = C (κ = -1) we will not get $n = k_-$. This is because the integral in (A.11) is singular for $j^2(B - A)\sin^2 q_k = k^2[(B - C) + (B - A)\sin^2 q_k]$ so that the solution in the κ = +1 limit will not go smoothly into the solution in the κ = -1 limit.

It is then desirable to seek a new momentum in which the quantization can be carried out. Define η^2 by

$$\eta^2 = (1 + \kappa)\, j_z^{\,2} - (1 - \kappa)\, j_x^{\,2} \tag{A.12}$$

so that the classical Hamiltonian becomes

$$H(j,m,\eta,q_j,q_m,q_\eta) = B\, j^2 - \frac{(A - C)}{2}\,\eta^2 \tag{A.13}$$

It is clear now that η^2 is conserved and that if we let $j^2 = \hbar^2 j(j+1)$ and $\nu^2 = \frac{\eta^2}{\hbar^2}$, the Hamiltonian is

$$H = bj\ (j + 1) - \frac{(a - c)}{2} \nu^2 \tag{A.14}$$

Comparing (A.14) with (A.7) it can be seen that ν is simply related to $E(\kappa)$ by

$$E(\kappa) = \kappa j\ (j + 1) - \nu^2 \tag{A.15}$$

In the limit of $\kappa = +1$, $j_x = \hbar k_+$, and in the limit $\kappa = -1$, $j_z = \hbar k_-$, so that η^2 has the correct behavior in the two limits. In order to transform from the k, q_k set to the η, q_η set we have that

$$\eta = (1 + \kappa)k^2 - (1 - \kappa)\ (j^2 - k^2)\ \sin^2 q_k \tag{A.16}$$

The F_2 generator that eliminates k in favor of η^2 is given by

$$F_2\ (j,\eta,q_j,q_k) = mq_m + jq_j + \int_0^{q_k} dx \sqrt{\frac{\eta^2 + (1 - \kappa)\ j^2\ \sin^2 x}{(1 + \kappa) + (1 - \kappa)\ \sin^2 x}} \tag{A.17}$$

Now η^2 has the dimensions of $(\text{momentum})^2$, but it can be seen from (A.12) that η^2 can take on either positive or negative values. The integral in (A.17) must be worked out separately for the two signs of η^2, and it will be seen that no logical inconsistencies result from allowing η^2 to be less than zero. Indeed, the case that $\eta^2 = 0$ is exactly the point at which (A.11) becomes discontinuous.

For the case that $\eta^2 > 0$ we have that

$$F_2\ (j,\eta,q_j,q_k) = mq_m + jq_j + \frac{\eta^2}{\sqrt{(1+\kappa)[\eta^2+j^2(1-\kappa)]}}\ \pi\left(\gamma, \frac{j^2(1-\kappa)}{\eta^2+j^2(1-\kappa)}, r\right) \tag{A.18a}$$

where

$$\sin^2\gamma = \frac{\sin^2 q_k[\eta^2+j^2(1-\kappa)]}{[\eta^2+j^2(1-\kappa)\sin^2 q_k]}$$

$$r^2 = \frac{(1-\kappa)}{(1+\kappa)}\;\frac{[j^2(1+\kappa) - \eta^2]}{[j^2(1-\kappa) + \eta^2]} \qquad \text{(A.18b)}$$

and $\Pi\,(\phi,n,k)$ is the elliptic integral of the third kind

$$\Pi\,(\phi,n,k) = \int_0^\phi \frac{d\alpha}{(1+n\sin^2\alpha)\sqrt{1-k^2\sin^2\alpha}}\;.$$

The coordinate conjugate to η is given by

$$q_\eta = \frac{\eta\,F(\gamma,r)}{\sqrt{(1+\kappa)[j^2(1-\kappa) + \eta^2]}} \qquad \text{(A.19)}$$

where $F(\phi,k) = \int_0^\phi \frac{d\alpha}{\sqrt{1-k^2\sin^2\alpha}}$ is the elliptic integral of the first kind and γ, r are the same as in (A.18b).

For $\eta^2 < 0$ not all values of q_k are classically allowed. Since k (η^2,q_k) is given by

$$k = \sqrt{\frac{\eta^2 + (1-\kappa)\,j^2\sin^2 q_k}{(1+\kappa) + (1-\kappa)\sin^2 q_k}} \qquad \text{(A.20a)}$$

and k must be real, we must have

$$\eta^2 + (1-\kappa)\,j^2\sin^2 q_k \geq 0 \qquad \text{(A.20b)}$$

If the integral in (A.17) is done considering the limits on q_k by (A.20b) we get for $\eta^2 < 0$

$$F_2(j,\eta,q_j,q_k) = m\, q_m + j\, q_j - \frac{\eta^2}{\sqrt{(1-\kappa)[(1+\kappa)j^2-\eta^2]}} \times \Pi\left(\gamma', \frac{j^2(1-\kappa)+\eta^2}{j^2(1-\kappa)}, r'\right) - F(\gamma', r') \tag{A.21}$$

where $r' = \frac{1}{r}$ and $\sin^2\gamma' = \frac{1}{\sin^2\gamma}$ [γ and r as in (A.18b)], and

$$q_\eta = \frac{\sqrt{-\eta^2}}{\sqrt{(1-\kappa)[j^2(1+\kappa) - \eta^2]}}\, F(\gamma',r') \tag{A.22}$$

The Eqs. (A.19) and (A.22) are all that is needed to apply classical S-matrix theory to collisions of an asymmetric rotor. The appropriate value of η^2 for a quantum state of the rotor can be obtained from the quantum mechanical values of $E(\kappa)$ by Eq. (A.15). Although there is now no need to obtain a semiclassical prediction of the energy levels, such a prediction is possible.

In order to quantize the asymmetric rotor semiclassically we use the Bohr-Sommerfeld quantization rule

$$2\pi\hbar(n + \alpha) = \oint \eta\, dq_\eta \tag{A.23}$$

where n is an integer and α is an arbitraty constant to be adjusted. The integral in (A.23) has parametric dependence on the energy and the magnitude of the angular momentum, which we take to be its quantum value $\hbar\sqrt{j(j+1)}$. Since η is a constant of the motion the integral is just the change in q_η over a complete cycle. Now if the left hand side of (A.23) is $2\pi\hbar\,(k_\pm + \alpha_\pm)$ for η^2 greater than or less than zero respectively, we get

$$\eta^2 > 0 : (1+\kappa)\,(k_+ + \alpha_+)^2 = \frac{4\,\nu^4\,K^2(m)}{\pi^2[j(j+1)(1-\kappa) + \nu^2]} \tag{A.24a}$$

and

$$\eta^2 < 0 : (1-\kappa)\,(k_- + \alpha_-)^2 = \frac{4\,\nu^4\,K^2\left(\frac{1}{m}\right)}{\pi^2[j(j+1)(1+\kappa) - \nu^2]} \tag{A.24b}$$

where $m = \dfrac{(1-\kappa)\,[j(j+1)(1+\kappa) - \nu^2]}{(1+\kappa)\,[j(j+1)(1-\kappa) + \nu^2]}$ and $K\,(m)$ is the complete elliptic integral of the first kind. By analogy with (A.12) it may be desirable to combine (A.24a) and (A.24b) by defining

$$N^2 = (1+\kappa)\,(k_{+1} + \alpha_+)^2 - (1-\kappa)\,(k_{-1} + \alpha_-)^2 \tag{A.25}$$

while letting ν^2 have the same sign as N^2. It can be seen that the difficulties in (A.11) arise where $\nu^2 = 0$ and that (A.24a) and (A.24b) pass smoothly through this boundary if (A.25) is used.

APPENDIX B. ACTION - ANGLE VARIABLES FOR ATOM - ASYMMETRIC ROTOR COLLISIONS

In this section, the conventions with regard to the rotor are the same as in Appendix A. Let $\vec{R}$ be the vector from the center of mass of the rotor to the atom, and α and β be the altitude and azimuth respectively of this vector. The Hamiltonian is

$$H = \frac{\mu}{2}\left(\dot{R}^2 + R^2\dot{\alpha}^2 + R^2\dot{\beta}^2 \sin^2\alpha\right) + \frac{I_x}{2}\left(\dot{\phi}\sin\theta\sin\psi + \dot{\theta}\cos\psi\right)^2$$

$$+ \frac{I_y}{2}\left(\dot{\phi}\sin\theta\cos\psi - \dot{\theta}\sin\psi\right)^2 + \frac{I_z}{2}\left(\dot{\phi}\cos\theta + \dot{\psi}\right)^2 + V(R,\gamma,\zeta) \quad \text{(B.1)}$$

where γ is the angle between $\vec{R}$ and the body fixed z axis and ζ is the angle between $\vec{R}$ and the body fixed x axis. Therefore

$$\cos\gamma = \cos\theta\cos\alpha + \sin\theta\sin\alpha\sin(\phi-\beta)$$

$$\cos\zeta = \sin\psi\left[\cos\alpha\sin\theta - \cos\theta\sin\alpha\sin(\phi-\beta)\right]$$

$$+ \cos\psi\sin\alpha\cos(\phi-\beta) \quad \text{(B.2)}$$

In terms of the canonical momenta H is

$$H = \frac{p_R^2}{2\mu} + \frac{p_\alpha^2}{2\mu R^2} + \frac{p_\beta^2}{2\mu R^2\sin^2\alpha} + \frac{A}{2}\left[p_\phi\frac{\sin\psi}{\sin\theta} + p_\theta\cos\psi - \frac{p_\psi\cos\theta\sin\psi}{\sin\theta}\right]^2$$

$$+ \frac{B}{2}\left[p_\phi\frac{\cos\psi}{\sin\theta} - p_\theta\sin\psi - p_\psi\frac{\cos\theta\cos\psi}{\sin\theta}\right]^2 + \frac{Cp_\psi^2}{2} + V(R,\gamma,\zeta) \quad \text{(B.3)}$$

where p_θ, p_ϕ, p_ψ are as in Appendix A and

$$p_R = \mu\dot{R}$$

$$p_\alpha = \mu R^2\dot{\alpha}$$

$$p_\beta = \mu R^2\sin^2\alpha\dot{\beta} \quad \text{(B.3a)}$$

(note that μ is the reduced mass of the "two-body" system where one body is the atom and the other is the rotor) Since ϕ and β only occur in the combination $(\phi-\beta)$, ϕ can be replaced by the new variable $\varepsilon = (\phi-\beta)$. This is done by the F_3 generator

$$F_3\ (\phi,\beta;\ \varepsilon,\beta) = -\beta p_\beta - \varepsilon p_\phi \tag{B.4}$$

which gives the new momenta $p_\varepsilon = p_\phi = m$ and $M = p_\varepsilon + p_\beta$, the projection of the total angular momentum on the space-fixed z axis. The orbital angular momentum ℓ is now introduced by an F_2 type generator using

$$\ell^2 = \frac{p\alpha^2}{2\mu R^2} + \frac{(M-m)^2}{2\mu R^2 \sin^2\alpha}$$

$$F_2(\varepsilon,\beta,\alpha;\ell,m,M) = m\varepsilon + \beta M + \ell \cos^{-1}\left[\frac{\ell\cos\alpha}{\sqrt{\ell^2-(M-m)^2}}\right] - (M-m)\cos^{-1}\left[\frac{(M-m)\cos\alpha}{\sin\alpha\sqrt{\ell^2-(M-m)^2}}\right] \tag{B.5}$$

The new coordinates are

$$\begin{aligned} q'_\ell &= \cos^{-1}\left[\frac{\ell\cos\alpha}{\sqrt{\ell^2-(M-m)^2}}\right] \\ Q_2 &= \beta - \cos^{-1}\left[\frac{(M-m)\cos\alpha}{\sin\alpha\sqrt{\ell^2-(M-m)^2}}\right] \\ Q_3 &= \varepsilon + \cos^{-1}\left[\frac{(M-m)\cos\alpha}{\sin\alpha\sqrt{\ell^2-(M-m)^2}}\right] \end{aligned} \tag{B.6}$$

The F_2 generator in Eq. (A6) is now used (with ϕ replaced by Q_3) and the new coordinates are

$$q_j' = \cos^{-1}\left[\frac{j^2 \cos\theta - mk}{\sqrt{j^2-k^2}\sqrt{j^2-m^2}}\right]$$

$$q_k = \psi - \cos^{-1}\left[\frac{k\cos\theta - m}{\sin\theta\sqrt{j^2-k^2}}\right]$$

$$q_m = Q_3 - \cos^{-1}\left[\frac{m\cos\theta - k}{\sin\theta\sqrt{j^2-m^2}}\right] \qquad \text{(B.7)}$$

The space fixed components of $\vec{j}$ and $\vec{\ell}$ are now given by

$$j_x = -\sin(Q_2 + q_m)\sqrt{j^2 - m^2}$$

$$j_y = \cos(Q_2 + q_m)\sqrt{j^2 - m^2}$$

$$j_z = m$$

$$\ell_x = -\cos Q_2\sqrt{\ell^2 - (M-m)^2}$$

$$\ell_{yz} = -\sin Q_2\sqrt{\ell^2 - (M-m)^2}$$

$$\ell_z = (M-m) \qquad \text{(B.8)}$$

so that the magnitude of the total angular momentum J is given by

$$J^2 = j^2 + \ell^2 + 2m(M-m) + 2\sqrt{j^2-m^2}\sqrt{\ell^2-(M-m)^2}\,\sin q_m \qquad \text{(B.9)}$$

It is now desired to replace m by J, and to express γ and ζ in terms of the final angle variables. The first is done with the generator

$$F_4\ (j,\ell,M,m;\ J,j,\ell,M)$$

$$= J\ \sin^{-1}\left[\frac{M(J^2+j^2-\ell^2)\ -\ 2m\ J^2}{\xi\sqrt{J^2-M^2}}\right] + \ell\ \sin^{-1}\left[\frac{m(J^2+\ell^2-j^2)-M(J^2-\ell^2-j^2)}{\xi\sqrt{\ell^2-(M-m)^2}}\right]$$

$$+ j\ \sin^{-1}\left[\frac{m(J^2+j^2-\ell^2)\ -\ 2Mj^2}{\xi\sqrt{j^2-m^2}}\right] + M\ \sin^{-1}\left[\frac{(J^2+j^2-\ell^2)\ -\ 2M(M-m)}{2\sqrt{J^2-M^2}\sqrt{\ell^2-(M-m)^2}}\right]$$

$$- m\ \sin^{-1}\left[\frac{(J^2-j^2-\ell^2)\ -\ 2m(M-m)}{2\sqrt{j^2-m^2}\sqrt{\ell^2-(M-m)^2}}\right] \tag{B.10}$$

where $\xi^2 = -J^4 - j^4 - \ell^4 + 2J^2j^2 + 2J^2\ell^2 + 2j^2\ell^2$

The new coordinates are

$$q_j = q'_j + \sin^{-1}\left[\frac{m(J^2+j^2-\ell^2)\ -\ 2Mj^2}{\xi\sqrt{j^2-m^2}}\right]$$

$$q_\ell = q'_\ell + \sin^{-1}\left[\frac{m(J^2+\ell^2-j^2)\ -\ M\ (J^2-\ell^2-j^2)}{\xi\sqrt{\ell^2-(M-m)^2}}\right]$$

$$q_M = Q_2 + \sin^{-1}\left[\frac{(J^2+\ell^2-j^2)\ -\ 2M\ (M-m)}{2\sqrt{J^2-M^2}\ \sqrt{\ell^2-(M-m)^2}}\right]$$

$$q_J - \sin^{-1}\left[\frac{M(J^2+j^2-\ell^2)\ -\ 2mJ^2}{\xi\ \sqrt{J^2-M^2}}\right] \tag{B.11}$$

Because of the overall rotational symmetry of the system, M can be set equal to zero without loss of generality. The two potential parameters are given in this set of coordinates and momenta by

$$\cos\gamma = \frac{\sqrt{j^2-k^2}}{j}\left[\cos q_\ell \cos q_j + \frac{(J^2-j^2-\ell^2)}{2\ell_j} \sin q_\ell \sin q_j\right]$$

$$+ \frac{k\,\xi \sin q_\ell}{2\ell j^2}$$

$$\cos\zeta = \frac{\sin q_k}{2\ell\sqrt{j^2-k^2}}\,[2\,\ell\,k\cos\gamma - \xi\sin q_\ell] + \cos q_k\,[\cos q_\ell \sin q_j$$

$$- \frac{(J^2-j^2-\ell^2)}{2\ell j}\sin q_\ell \cos q_j] \qquad (B.12)$$

The Hamiltonian is now given by

$$H = \frac{p_R^{\ 2}}{2\mu} + \frac{\ell^2}{2\mu R^2} + j^2\,[A\sin^2 q_k + B\cos^2 q_k] + k^2\,[C - A\sin^2 q_k - B\cos^2 q_k]$$

$$+ V\,(R,\gamma,\zeta) \qquad (B.13)$$

APPENDIX C. MONTE - CARLO TECHNIQUE FOR ASYMMETRIC ROTOR TRANSITIONS

Principally because the second "quantum number", ν, for defining the state of the asymmetric rotor is not an integer, and may be imaginary, several modifications must be made in the standard Monte-Carlo classical trajectory technique for evaluating the cross sections. The classical S-matrix result for the total cross section (see Eqs. 3.1 and 3.2) is given by

$$\sigma_{j_2\nu_2\leftarrow j_1\nu_1}(E) = \frac{\pi\hbar^2}{(2\mu E)\ (2j_1+1)}\sum_{J=0}^{\infty}(2\ J+1)\sum_{\ell_1,\ell_2}\left|S^J_{\ell_2 j_2\nu_2,\ell_1 j_1\nu_1}\right|^2 \qquad (\mathrm{C.1})$$

where $$S^J_{\ell_2,j_2,\nu_2;\ell_1,j_1,\nu_1}(E) = \left[(-2\pi i\hbar)^3\,\frac{\partial(\ell_2,j_2,\nu_2)}{\partial(q_{\ell_1},q_j,q_{\nu_1})}\right]^{\frac{1}{2}} e^{i\phi(\ell_2,j_2,\nu_2;\ell_1,j_1,\nu_1)/\hbar} \qquad (\mathrm{C.2})$$

Equation C.1 is transformed to a form suitable for Monte-Carlo evaluation by ignoring the phase in (C.2) and averaging over final quantum numbers so that the Jacobian factor in (C.2) cancels out.

We first approximate the infinite sum over ℓ_2 by an integral over ℓ_2. If this integral is then transformed into an integral over d q_ℓ, the factor $\left(\frac{\partial\ell_2}{\partial q_{\ell_1}}\right)$ which arises cancels with the Jacobian in the square of the S-matrix element. We now have

$$\sigma_{j_2,\nu_2\leftarrow j_1,\nu_1}(E) = \frac{\pi\hbar^2}{2\mu E(2j_1+1)}\sum_{J=0}^{\infty}(2J+1)\sum_{\ell_1}\int_0^1 d\left(\frac{q_{\ell_1}}{2\pi}\right)\frac{1}{(2\pi\hbar)^2} \times\left[\frac{\partial(j_2,\nu_2)}{\partial(q_{j_1},q_{\nu_1})}\right]^{-1} \qquad (\mathrm{C.3})$$

To complete remove the Jacobian we want to average j_2 and ν_2 over "quantum number" intervals. This is straightforward for j_2 but not for ν_2 since this is non-integer for the desired final state and may be imaginary. Because of this last difficulty we average over a ν_2^2 interval rather than a ν_2 interval and take the averages of the ν^2 values for the various states as the endpoints.

We now have

$$\sigma_{j_2,\nu_2 \leftarrow j_1,\nu_1}(E) = \frac{\pi\hbar^2}{2\mu E(2j_1+1)} \sum_{J=0}^{\infty} (2J+1) \sum_{\ell_1=|J-j_1|}^{J+j_1} \int_{j2-\frac{1}{2}}^{j2+\frac{1}{2}} \int_{\nu_{low}^2}^{\nu_{top}^2} d(\nu_2^2) \int_0^1 d\left(\frac{q_{\ell_1}}{2\pi}\right)$$

$$\times \frac{1}{(\nu_{top}^2 - \nu_{low}^2)} \frac{1}{(2\pi\hbar)^2} \left[\frac{\partial(j_2,\nu_2)}{\partial(q_{j_1},q_{\nu_1})}\right]^{-1} \qquad (C.4)$$

where ν_{top}^2 and ν_{low}^2 are the endpoints of the ν^2 interval. It is now desired to cancel out the Jacobian entirely by changing the integrals over j_2 and ν_2^2 to integrals over q_{j_1} and q_{ν_1}.

Since it is more convenient to compute the trajectories in the k,q_k set of canonical variables rather than the ν,q_ν set, we would like expression to involve only the former set. From the results in Appendix A we have that

$$\frac{\partial q_{\nu_1}}{\partial q_{k_1}} = \frac{\nu_1}{\sqrt{(1+\kappa) + (1-\kappa)\sin^2 q_k}\,\sqrt{\nu_1^2 + j_1(j_1+1)(1-\kappa)\sin^2 q_{k_1}}} \qquad (C.5)$$

so that $\int d(\nu_2^2) = 2\nu_2 \int d\nu_2 = 2\nu_2 \int \frac{\partial \nu_2}{\partial q_{\nu_1}} \, dq_{\nu_1}$

$$= 2\nu_2 \int \left(\frac{\partial \nu_2}{\partial q_{\nu_1}}\right)\left(\frac{\partial q_{\nu_1}}{\partial q_{k_1}}\right) dq_{k_1}$$

If we insert a function χ that is one if a trajectory falls in the appropriate j_2, ν_2^2 "box" and zero otherwise we get finally

$$\sigma_{j_2,\nu_2 \leftarrow j_1,\nu_1}(E) = \frac{\pi \hbar^2 \nu_1}{2\mu E \, (2j_1+1) \, \Delta} \sum_{J=0}^{\infty} \sum_{\ell_1=|J-j_1|}^{J+j_1} \int_0^1 d\left(\frac{q_{\ell_1}}{2\pi}\right) \int_0^1 \left(\frac{q_{j_1}}{2\pi}\right) \int_0^1 d\left(\frac{q_{k_1}}{2\pi}\right)$$

$$\times \frac{\chi \, \nu_2}{\sqrt{(1+\kappa) + (1-\kappa)\sin^2 q_{k_1}} \, \sqrt{\nu_1^2 + j_1(j_1+1)\,(1-\kappa)\sin^2 q_{k_1}}} \qquad \text{(C.6)}$$

where Δ is the length of the ν_2^2 "box". Eq. (C.6) is now in a form amenable to Monte-Carlo evaluation and is the desired result.

TABLE I. Values of Parameters Chosen for the Model Potential

Atom	F_i (Hartrees)	S_i (a_o^2)
O	1.0	0.88333
C	1.0	0.970
$H_{1,2}$	1.0	0.75667

TABLE II. Formaldehyde Energy Levels[a]

State ($J_{k_-k_+}$)	E (°K)	$\nu^2 = \frac{\eta^2}{\hbar^2}$
0_{00}	0	0
1_{01}	3.49579	0.03894
1_{11}	15.17141	-1.92213
1_{10}	15.40323	-1.96106
2_{02}	10.48396	0.11738
2_{12}	21.93119	-1.80532
2_{11}	22.62663	-1.92213
2_{21}	57.65349	-7.80532
2_{20}	57.65691	-7.80590

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11. The standard ordering of rotational constants as indicated at the beginning of Section II would make the C-O axis the x axis of the molecule. The component of $\vec{j}$ on this axis (k' of Eq. (2.3b)) is thus a nearly conserved quantity. For mathematical simplicity, the CO axis will be taken to be the body fixed z axis in the remainder of this section so that the prime on k' will be dropped.
12. In this set of coordinates and momenta a typical trajectory required 0.12 seconds of computer time on a CDC 7600.
13. For a more detailed discussion of the term "classically allowed", see ref. 6a.
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FIGURE CAPTIONS

Figure 1. (a) The geometry of formaldehyde; see ref. 8.

(b) The coordinate system for formaldehyde.

Figure 2. Cross sections for the indicated rotational excitations in H_2 (spherically symmetric) + H_2CO collisions as a function of initial relative translational energy. The solid lines are the results of the Monte Carlo classical trajectory calculations and the points the semiclassical values; the solid (open) points correspond to the upper (lower) curve. The energetic threshold for all four transitions is 7°K ± ∿ .5°K (see Table II).

Figure 3. (a) Cross section for the $1_{11} \to 1_{10}$ (and essentially also the $1_{10} \to 1_{11}$) transition in collisions H_2 and H_2CO, as a function of initial translational energy.

(b) The cross section ratio, defined by Eq. (4.2), as a function of initial translational energy.

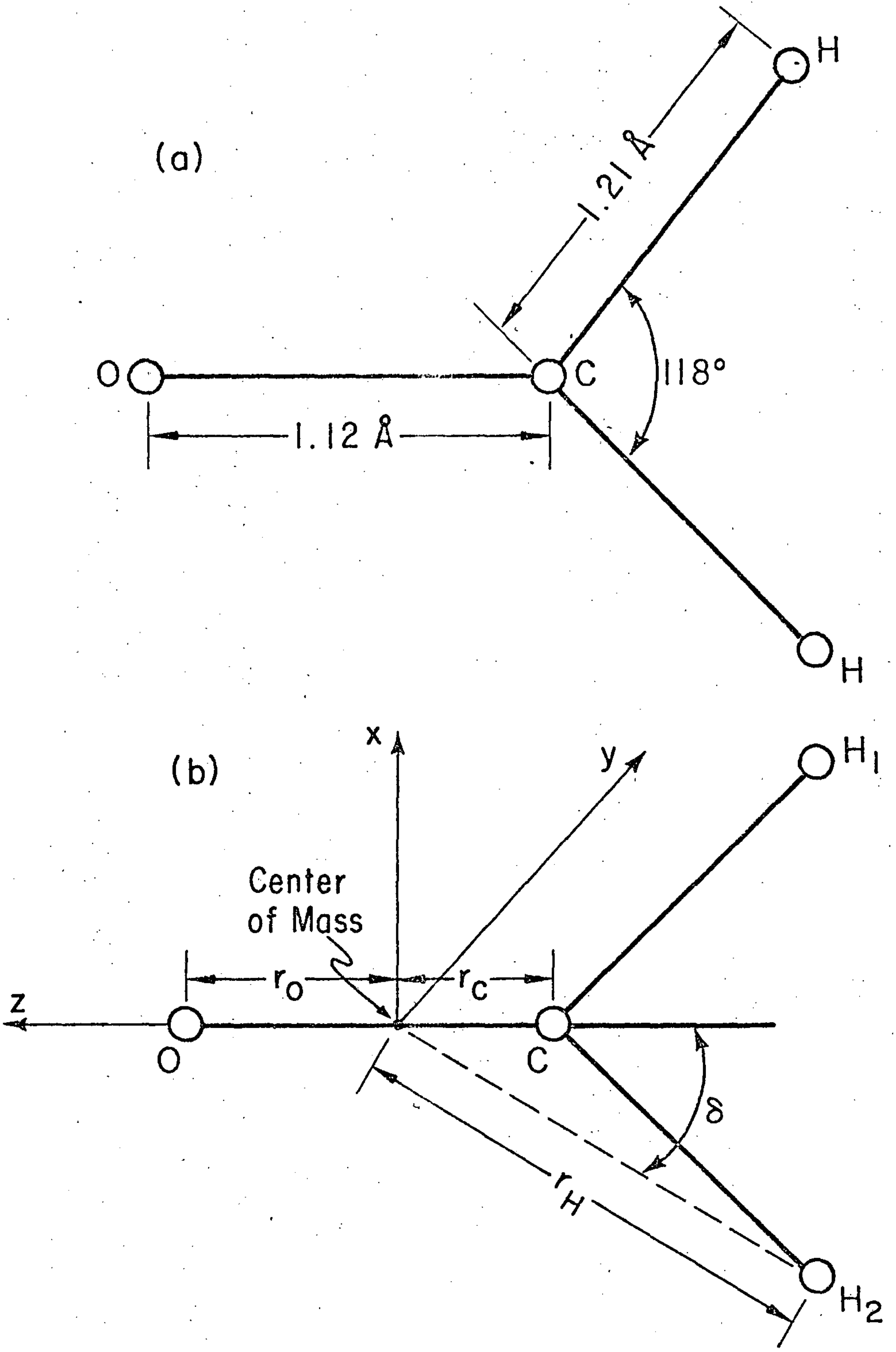

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Fig. 1

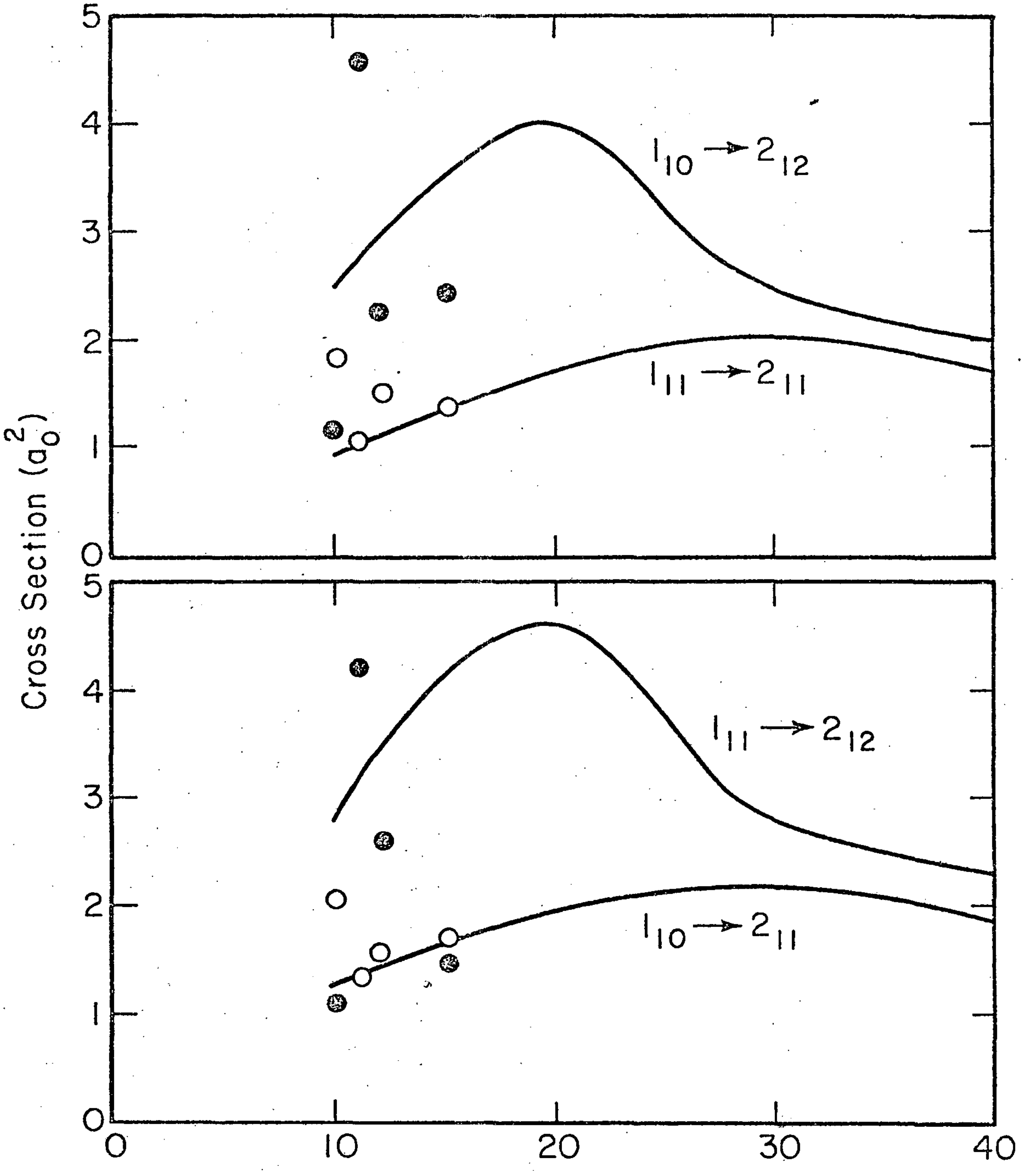

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Fig. 2

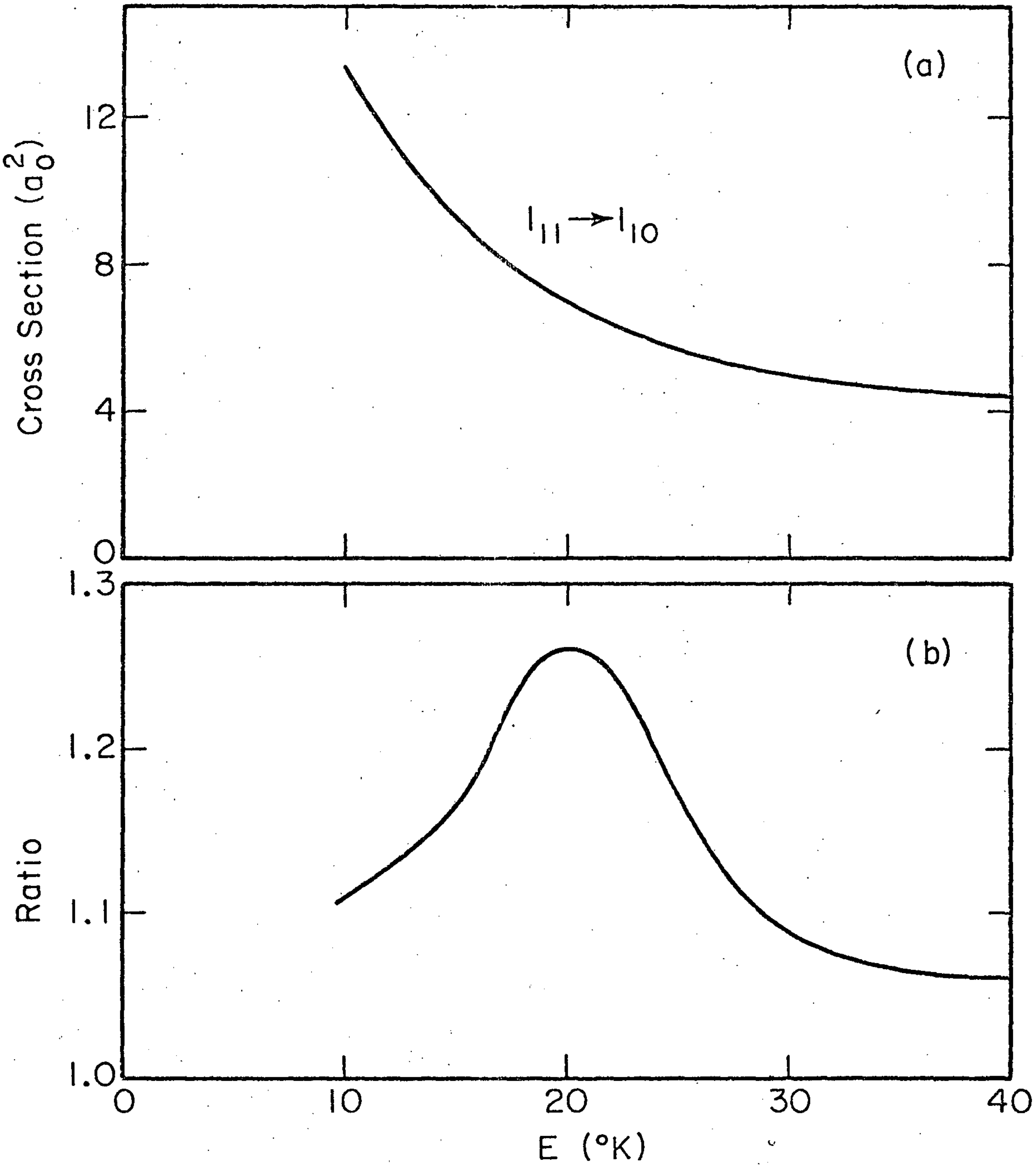

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Fig. 3

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