Semiclassical treatment of atom–asymmetric rotor collisions; rotational excitation of formaldehyde at low energies

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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 to 150 K. Classical Monte Carlo trajectory calculations were also carried out for the same system in the energy range 10–40 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 (11) has a population greater than would be expected if the system were in equilibrium with the background radiation. Townes and Cheung 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 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 and by application of “classical S-matrix” theory, a semiclassical approach that uses numerically computed classical trajectories in combination with essential quantum mechanical features. A number of applications 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 Sec. 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 Sec. IV.

II. SEMICLASSICAL DESCRIPTION OF THE ISOLATED ASYMMETRIC ROTOR

In order to apply classical S-matrix theory to bimolecular collision processes 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 with principal moments of inertia $I_x$, $I_y$, $I_z$ such that $I_x \geq I_y \geq I_z$. Letting $A = 1/2I_y$, $B = 1/2I_x$, $C = 1/2I_z$, the asymmetry parameter $\kappa$ is defined by

$$\kappa = \frac{2B - A - C}{A - C}. \quad (2.1)$$

For a prolate symmetric top $I_x = I_y$ and $\kappa = -1$, while for an 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 (see Appendix A for more details)

$$H(j, m, k; q, \eta, \phi) = B(j^2 - k^2) \cos^2 \phi + A(j^2 - k^2) \sin^2 \phi + Ck^2. \quad (2.2)$$

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

$$H(j, m, k; q, \eta, \phi) = B(j^2 - k^2) - (B - C)k^2. \quad (2.3a)$$
In the prolate symmetric rotor limit \((B = C)\), one needs to define \(k^*\) to be the projection of \(J\) along the body-fixed \(x\) axis, and the Hamiltonian then becomes
\[
H(j, \nu, q_m, q_\nu) = B(J^2 - k^* + \nu^2) + (A - B)k^{*2}.
\]
(2.3a)

Since (2.2) has no dependence on \(q_m\) or \(q_\nu\), 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 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
\[
H_j(k, q_\nu) = (J^2 - k^2)(A \sin^2 q_\nu + B \cos^2 q_\nu) + Ck^2.
\]

One then applies the Bohr–Sommerfeld quantum condition to this one-dimensional system in order to quantize the \(k\) degree of freedom:
\[
2\pi \hbar(n + \frac{1}{2}) = \oint dq_\nu k(q_\nu, J, E),
\]
(2.4)
where \(k(q_\nu, J, E)\) is determined from the Hamiltonian by conservation of energy:
\[
k(q_\nu, J, E) = \sqrt{\frac{E - J^2(A \sin^2 q_\nu + B \cos^2 q_\nu)}{C - A \sin^2 q_\nu - B \cos^2 q_\nu}}.
\]
(2.5)

Equation (2.4) can now in principle be inverted to give \(E(j, \nu)\). 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 \(\eta\) by
\[
\eta^2 = (1 + \kappa)J^2 - (1 - \kappa)J^2,
\]
(2.6)
where \(J_x\) and \(J_y\) are the components of \(J\) along the corresponding body-fixed axes. It may be noted that in the oblate limit \((\kappa = 1)\), \(\eta^2 = 2J^2\), and in the prolate limit \((\kappa = -1)\), \(\eta^2 = -2J^2\). The classical Hamiltonian in terms of this new variable is given by
\[
H(j, \eta, q_j, q_\eta) = BJ^2 - \frac{1}{2}(A - C)\eta^2
\]
(2.7a)
so that \(\eta^2\) is a constant of the motion. If one lets \(J^2 = \hbar^2(j + 1)\), \(\nu^2 = \eta^2/\hbar^2\), \(a = \hbar^2A\) etc., then (2.7a) becomes
\[
H = bj(j + 1) - \frac{1}{2}(a - c)\nu^2,
\]
(2.7b)
so that \(\nu\) is related to the quantum mechanical quantity \(E(\kappa)\) by
\[
\nu^2 = k^2/J(j + 1) - \nu^2.
\]
(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 \(\nu\) (determined from tabulated values of \(E(\kappa)\)). Appendix A carries out the canonical transformations necessary to replace \(k\) by \(\eta\).

### III. SEMICLASSICAL THEORY OF ATOM-ASYMMETRIC ROTOR COLLISIONS

The cross section for the inelastic process
\[
\text{CH}_2\text{O}(j_1, \nu_1) + \text{H}_2 \rightarrow \text{CH}_2\text{O}(j_2, \nu_2) + \text{H}_2
\]
is given by
\[
\sigma_{\text{ip}_2} = \frac{n\hbar}{(2\mu E)(2j_1 + 1)} \times \frac{b}{\hbar} \sum_{l_1 l_2} \sum_{l_1 \nu_1} \left| S_{\text{ip}_2 l_1 l_2 \nu_1 \nu_2} \right|^2,
\]
(3.1)
where \(l\) is the orbital angular momentum quantum number for relative translation of the collision partners, \(j\) and \(\nu\) are the quantities that define the rotational state of the isolated formaldehyde as in Eq. (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 \(\mu\) 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, except that here \(\nu\) 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. Again, the expression is of the same form as that for the atom–diatom rotational–vibrational system.

\[
S_{\text{ip}_2 l_1 l_2 \nu_1 \nu_2}(E) = \sum (-2\pi i)^3 \frac{\delta(l_2 j_2, \nu_2)}{\delta(1, q_1, q_{\nu_1})} 1^{-1/2} \left[ a(l_2 j_2, \nu_2) \right] [b(l_1 j_1, \nu_1) / \hbar],
\]
(3.2)
where the sum indicates a sum of such terms for all trajectories which obey the correct initial and final boundary conditions (see Refs. 5 and 10 for more details).

In order to use Eqs. (3.1) and (3.2) it is necessary that \(J^2\) be quantized everywhere and that \(j^2, l^2, \) and \(\nu^2\) be quantized in the initial and final asymptotic regions. \(J^2\) and \(l^2\) are quantized by the usual Langer prescription,
\[
\begin{align*}
J^2 &= \hbar^2(\frac{I + \frac{1}{2}}{2}), \\
\nu^2 &= \hbar^2(\frac{\nu}{2}),
\end{align*}
\]
(3.3)
\(\nu^2\) is "quantized" by setting it equal to the value determined from Eq. (2.8) by \(j\) and the quantum value of \(E(\kappa)\). The quantum mechanical quantization of \(j^2\) (i.e., \(j^2 \rightarrow \hbar^2(j + 1)\)) 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 \(I, j, \nu, q_1, q_\nu, q_j\) 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. Since the relationship between $k$ and $\eta$ is also not very tractable (see Appendix A), it was decided to compute the trajectories in the $l$, $j$, $k$, $q_l$, $q_j$, $q_k$ 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

$$H(p_R, l, j, k; R, q_l, q_j, q_k)$$
$$= \frac{p_R^2}{2\mu} + \frac{l^2}{2\mu R^2} + j^2[C \sin^2 q_k + B \cos^2 q_k]$$
$$+ \hbar^2(A - B \cos^2 q_k - C \sin^2 q_k) + V(R, \gamma, \zeta),$$

(3.4)

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

A model potential of the form

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

(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 which were in progress at the time this work was begun. The sum is over the four atoms making up the formaldehyde and $R_i$ is the square of the distance between the $i$th 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. Since the quantity of interest for the present astrophysical problem is the relative size of cross sections (see Sec. IV), however, it may be that the detailed form of the potential beyond that which essentially determines the size and shape of the molecules will not seriously alter the major results. Work currently in progress (B. J. Garrison, H. F. Schaefer, W. A. Lester, and W. H. Miller) on the potential surface for helium–formaldehyde should provide a much more realistic interaction potential.

The structure of formaldehyde given in Ref. 8 was adopted for this work since it is the same as that used in Refs. 2 and 3. The values given\(^8\) for the rotational constants are $A_0 = 282.106$, $B_0 = 38.834$, and $C_0 = 34.004$ MHz, which correspond to an asymmetry parameter $\kappa$ of ~0.9610644. The adopted structure and the coordinate system used are shown in Fig. 1. The values of the structural parameters with respect to the center of mass as shown in Fig. 1(b) are then $r_0 = 0.9443a_0$, $r_1 = 1.2925a_0$, $r_2 = 2.9948a_0$, $\delta = 37.29^\circ$. The energies and value of $\nu$ 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 $(R, \gamma, \zeta)$ by

\begin{table}
\begin{tabular}{|c|c|c|}
\hline
State $(\lambda, \mu)_{ij}$ & $E$ ($\Delta$) & $\nu^2 = \eta^2 + \zeta^2$ \\
\hline
$0_0$ & 0 & 0 \\
$1_{21}$ & 3,49579 & 0,03894 \\
$3_{11}$ & 0,32213 \\
$4_{10}$ & 21,30326 & 1,96106 \\
$3_{01}$ & 10,48396 & 0,11738 \\
$5_{00}$ & 2,9948a_0 & 0,3729 \\
$7_{11}$ & 22,62663 & 1,2925 \\
$6_{11}$ & 57,65349 & 7,80532 \\
$8_{22}$ & 57,6691 & 7,80590 \\
\hline
\end{tabular}
\end{table}
\[ R_0^2 = R^2 + r_0^2 - 2R r_0 \cos \gamma, \]
\[ R_0^2 = R^2 + r_0^2 + 2R r_0 \cos \gamma, \]
\[ R_{11} = R^2 + r_{11}^2 + 2R r_{11} (\sin \delta \cos \zeta - \cos \delta \cos \zeta), \]
\[ R_{10} = R^2 + r_{10}^2 - 2R r_{10} (\sin \delta \cos \zeta + \cos \delta \cos \zeta). \]

Even at the low collision energies employed the excitation of the \( j = 1 \) states to \( j = 2 \) states is a "classically allowed" 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 eight 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 not to use the "primitive" semiclassical expression (3.2), but rather the appropriate uniform asymptotic expression.\(^6\)\(^6\)\(^6\)\(^14\)\(^14\) The semiclassical results discussed in Sec. IV have all been "uniformized" in this way.

For the Monte Carlo trajectory calculations it was decided to modify the standard procedures\(^1\) somewhat because only a few values of \( J, l_1, \) and \( l_2 \) contribute to the sums in Eq. (3.1) at those low collision energies. Proceeding along the lines of Ref. 8(c), therefore, \( J \) and \( l \) 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 Fig. 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 \(^\circ\)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,\(^5\) 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 3(a) shows the classical Monte Carlo results for the \( 1_{11} - 1_{10} \) cross section as a function of collision energy \( E \). Since microscopic reversibility implies that

\[ \sigma(1_{11} - 1_{10}) = \frac{E}{E - \Delta \epsilon} \sigma(1_{10} - 1_{11}), \]

where \( \Delta \epsilon \) is the splitting of the \( 1_{11} \) and \( 1_{10} \) levels, \( \Delta \epsilon = 0.23182 \) \(^\circ\)K, the cross sections for the \( 1_{10} - 1_{11} \) and \( 1_{11} \)
−1_{10} transitions are essentially equal at the energies E considered.

Although a number of additional complications 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_{21} → 1_{11} and 2_{11} → 1_{10}) were infinitely fast compared to inelastic collision rates, and if the radiative rates between the 1_{11} and 1_{10} states were negligibly slow, then simple considerations imply that the steady-state ratio R of population of the 1_{11} state to that of the 1_{10} state would be

\[ R = \frac{\sigma(1_{11} - 1_{10}) + \sigma(2_{21} - 1_{10})}{\sigma(1_{10} - 1_{11}) + \sigma(2_{11} - 1_{11})}. \]  

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

\[ R = \exp(\Delta E/kT). \]  

R = 1.1 and 1.2, for example, imply temperatures 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 the R versus E relation in Fig. 3(b)—this is in good qualitative agreement with the observed population ratio corresponding to T ~ 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_{21} level is favored over that to the 2_{11} level, in accord with Townes and Cheung, 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 \( x, y, \) and \( z \) be the principal axes of the molecule with \( L_x = L_y = L_z \). For a prolate symmetric top \( L_x = L_y \) and for an oblate symmetric top \( L_x = L_y \). The classical Hamiltonian is

\[ H = \frac{1}{2} L_x \omega_x^2 + \frac{1}{2} L_y \omega_y^2 + \frac{1}{2} L_z \omega_z^2, \]  

where \( \omega_x \) are the angular velocities about the appropriate axes. Now introducing the Euler angles \( \theta, \phi, \psi \) of the body, we have

\[ \omega_x = \dot{\psi} \sin \theta \sin \psi + \dot{\theta} \cos \phi \sin \psi, \]
\[ \omega_y = \dot{\phi} \sin \theta \cos \psi - \dot{\theta} \sin \psi, \]
\[ \omega_z = \dot{\psi} \cos \theta + \dot{\phi}, \]

so that

\[ p_x = I_x \omega_x = p_y \sin \theta \sin \psi + I_y \omega_y \sin \theta \cos \psi + I_z \omega_z \cos \theta, \]
\[ p_y = I_x \omega_x \cos \phi - I_y \omega_y \sin \phi, \]
\[ p_z = I_z \omega_z, \]

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

\[ j_z = \frac{p_x \sin \psi}{\sin \theta} + p_y \cos \phi - \frac{p_z \cos \theta \sin \psi}{\sin \theta}, \]
\[ j_y = \frac{p_x \cos \psi}{\sin \theta} - p_y \sin \phi - \frac{p_z \cos \theta \cos \psi}{\sin \theta}, \]

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

\[ H(\theta, \phi, \psi, p_x, p_y, p_z) = A \left( \frac{p_x \sin \psi}{\sin \theta} + p_y \cos \phi - \frac{p_z \cos \theta \sin \psi}{\sin \theta} \right)^2 + B \left( \frac{p_x \cos \psi}{\sin \theta} - p_y \sin \phi - \frac{p_z \cos \theta \cos \psi}{\sin \theta} \right)^2 + C p_z^2, \]

where \( A = 1/2 I_z, \) \( B = 1/2 I_y, \) \( C = 1/2 I_x \) and the square of the magnitude of the angular momentum is

\[ j^2 = j_x^2 + j_y^2 + j_z^2 = p_x^2 + (1/\sin^2 \theta)(p_y^2 + p_z^2 - 2 p_x p_z \cos \theta). \]

The asymmetry parameter \( \kappa \) is defined by \( \kappa = (2B - A - C)/(A - C) \) 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

\[ 2E = (a + c) j(j + 1) + (a - c) E(\kappa), \]

where \( a = \hbar^2 A, \) etc.

We now eliminate \( p_x \) in favor of \( j, \) the magnitude of the rotational angular momentum by a canonical transformation using an F_2 generator. This generator is

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

where \( m = p_x \) is the component of \( j \) along the space-fixed z axis and \( k = p_z \) is the component of \( j \) 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

\[ q_j = \cos^{-1} \left( \frac{\cos \theta - k}{\sin \theta (j^2 - m^2)^{1/2}} \right), \]
\[ q_m = \phi - \cos^{-1} \left( \frac{\cos \theta - m}{\sin \theta (j^2 - m^2)^{1/2}} \right). \]
\[ a_k = \psi - \cos^{-1} \left( \frac{k \cos \theta - m}{\sin \theta} \right) \sin (j^2 - k^2)^{1/2} \]

\[ H(j, k, m, q, q_k, q_m) = j^2 (A \sin^2 q_a + B \cos^2 q_a) + k^2 (C - A \sin^2 q_a - B \cos^2 q_a) \]

\[ (A10) \]

Since \( q_a \) 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 (A10) that we have an effectively one-dimensional problem and that the semicircular energy levels might be calculated by applying the Bohr–Sommerfeld quantization rules to the \( k, q_a \) system (with \( j \) as a constant parameter). This would give

\[ 2\pi \hbar (n + \frac{1}{2}) = \int_0^{2\pi} dq_a \left( \frac{E - j^2 (A \sin^2 q_a + B \cos^2 q_a)}{C - A \sin^2 q_a - B \cos^2 q_a} \right)^{1/2} \]

\[ (A11) \]

with \( j^2 = h^2 j(j + 1) \). In the limit \( A = B (k = +1) \) we would get the correct quantum result that \( n = k \) but in the limit \( B = C (k = -1) \) we will not get \( n = k \). This is because the integral in (A11) is singular for

\[ j^2 (B - A \sin^2 q_a) = k^2 (B - C + (B - A \sin^2 q_a)) \]

so that the solution in the \( k = +1 \) limit will not be smoothly into the solution in the \( k = -1 \) limit.

It is thus desirable to seek a new momentum in which the quantization can be carried out. Define \( \eta \) by

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

so that the classical Hamiltonian becomes

\[ H(j, m, q, q_k, q_m) = B j^2 - \frac{\hbar^2}{2} (A - \eta^2) \]

\[ (A12) \]

It is clear now that \( \eta^2 \) is conserved and that if we let \( j^2 = \hbar^2 (j_1 + 1) \) and \( \eta^2 = \hbar^2 \eta^2 \), the Hamiltonian is

\[ H = B j (j_1 + 1) - \frac{\hbar^2}{2} (A - \eta^2) \]

\[ (A13) \]

Comparing (A14) with (A7) it can be seen that \( \nu \) is simply related to \( E(\kappa) \) by

\[ E(\kappa) = \kappa j (j + 1) - \nu^2 \]

\[ (A15) \]

In the limit of \( \kappa = +1 \), \( j_1 = \hbar j \), and in the limit \( \kappa = -1 \), \( j_1 = \hbar j \), so that \( \eta^2 \) has the correct behavior in the two limits. In order to transform from the \( k, q_a \) set to the \( \eta, q_a \) set we have that

\[ \eta = \frac{1}{(1 + \kappa)} j^2 - \frac{1}{(1 - \kappa)} (j^2 - k^2) \sin^2 q_a \]

\[ (A16) \]

The \( F_2 \) generator that eliminates \( k \) in favor of \( \eta^2 \) is given by

\[ F_2(j, \eta, q, q_k) = m q_a + \frac{\eta^2}{(1 + \kappa)} j^2 \sin^2 x \]

\[ + \int_0^{aq_a} \left( \frac{\eta^2 + j^2 - \eta_j^2}{(1 + \kappa)} \right) \sin^2 x \]

\[ (A17) \]

Now \( \eta^2 \) has the dimensions of momentum squared, but it can be seen from (A12) that \( \eta^2 \) can take on either positive or negative values. The integral in (A17) must be worked out separately for the two signs of \( \eta^2 \) and it will be seen that no logical inconsistencies result from allowing \( \eta^2 \) to be less than zero. Indeed, the case that \( \eta^2 = 0 \) is exactly the point at which (A11) becomes discontinuous.

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

\[ F_2(j, \eta, q, q_k, q_m) = m q_a + j q_j \]

\[ + \frac{\hbar^2}{(1 + \kappa)} \left( \frac{\eta^2 + j^2 - \eta_j^2}{(1 + \kappa)} \right)^{1/2} \]

\[ \times \left( \gamma, \frac{\eta_j^2 (1 - \kappa)}{\eta^2 (1 + \kappa)}, \eta_j^2 \right) \]

\[ (A18a) \]

where

\[ \sin \gamma \]

\[ \sin \gamma = \frac{\sin \gamma}{\sin \gamma (1 + \kappa)} \sin \gamma (1 - \kappa) \]

\[ \gamma = \frac{(1 - \kappa)}{(1 + \kappa)} \left( \frac{j^2 (1 + \kappa) - \eta^2}{j^2 (1 + \kappa) + \eta^2} \right) \]

\[ \times \left( \gamma, \frac{\eta_j^2 (1 - \kappa)}{\eta^2 (1 + \kappa)}, \gamma \right) \]

\[ \right) \]

\[ (A18b) \]

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

\[ \Pi(\phi, n, k) = \int_0^\phi \frac{d\alpha}{(1 + n \sin^2 \alpha)(1 - k^2 \sin^2 \alpha)^{1/2}} \]

\[ (A19) \]

The coordinate conjugate to \( \eta \) is given by

\[ q_a = \frac{\eta F(\gamma, \gamma)}{((1 + \kappa) j^2 (1 + \kappa) + \eta_j^2)^{1/2}} \]

\[ (A20a) \]

where

\[ F(\phi, k) = \int_0^\phi \frac{d\alpha}{(1 - k^2 \sin^2 \alpha)^{1/2}} \]

is the elliptic integral of the first kind, and \( \gamma \) and \( \gamma \) are the same as in (A18b).

For \( \eta < 0 \) not all values of \( q_a \) are classically allowed. Since \( h(\eta, q_a) \) is given by

\[ \eta = \frac{(\eta_j^2 + (1 + \kappa) j^2 \sin^2 q_a)}{(1 + \kappa) + (1 + \kappa) \sin^2 q_a} \]

\[ (A20a) \]

and \( k \) must be real, we must have

\[ \eta^2 + (1 - \kappa) j^2 \sin^2 q_a \leq 0 \]

\[ (A20b) \]

If the integration in (A17) is done considering the limits on \( q_a \) by (A20b) we get for \( \eta^2 < 0 \)

\[ F_2(j, \eta, q, q_k) = m q_a + j q_j - \frac{\eta^2}{((1 - \kappa) j^2 - \eta_j^2)^{1/2}} \]

\[ \left( \gamma, \frac{\eta_j^2 (1 - \kappa)}{\eta^2 (1 + \kappa)}, \gamma \right) - F(\gamma, \gamma) \]

\[ (A21) \]

where \( \gamma = 1/\gamma \) and \( \sin^2 \gamma = 1/\sin^2 \gamma \) [\( \gamma \) and \( \gamma \) as in (A18b)], and

\[ q_a = \frac{-\eta^2 \gamma}{((1 - \kappa) j^2 (1 + \kappa) - \eta_j^2)^{1/2}} \gamma \]

\[ (A22) \]

Equations (A19) and (A22) are all that is needed to apply classical S-matrix theory to collisions of an asymmetric rotor. The appropriate value of \( \eta^2 \) for a quantum state of the rotor can be obtained from the quantum mechanical values of \( E(\kappa) \) by Eq. (A15). 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

\[ 2\pi R(n + \alpha) = \int \eta dq_a \]

\[ (A23) \]
pendence on the energy and the magnitude of the angular momentum, which we take to be its quantum value
\( \hbar (j+1)^{\frac{3}{2}} \). Since \( \eta \) is a constant of the motion the integral is just the change in \( q_x \) over a complete cycle. Now if the left-hand side of (A23) is \( 2\pi \hbar (k_x+\alpha_x) \) for \( \eta^2 \) greater than or less than zero, respectively, we get
\[
(1+\kappa)(k_x+\alpha_x)^2 = \frac{4\nu^4K^2(m)}{\pi^2(j+1)(1+\kappa)-\nu^2} \eta^2 > 0 \quad (A24a)
\]
and
\[
(1-\kappa)(k_x+\alpha_x)^2 = \frac{4\nu^4K^2(1/m)}{\pi^2(j+1)(1-\kappa)-\nu^2} \eta^2 < 0 \quad (A24b)
\]
where
\[
m = \frac{(1-\kappa)(j+1)(1+\kappa)-\nu^2}{(1+\kappa)(j+1)(1-\kappa)+\nu^2}
\]
and \( K(m) \) is the complete elliptic integral of the first kind. By analogy with (A12) it may be desirable to combine (A24a) and (A24b) by defining
\[
N^2 = (1+\kappa)(k_x+\alpha_x)^2 -(1-\kappa)(k_x+\alpha_x)^2
\]
while letting \( \nu^2 \) have the same sign as \( N^2 \). It can be seen that the difficulties in (A11) arise where \( \nu^2 = 0 \) and that (A24a) and (A24b) pass smoothly through this boundary if (A25) is used.

APPENDIX B: ACTION–ANGLE VARIABLES FOR ATOM–ASYMMETRIC ROTOR COLLISIONS

In this appendix, the conventions with regard to the rotor are the same as in Appendix A. Let \( R \) be the vector from the center of mass of the rotor to the atom, and \( \alpha \) and \( \beta \) be the altitude and azimuth respectively of this vector. The Hamiltonian is
\[
H = \frac{1}{2}(\dot{R}^2 + R \ddot{R}^2 + R^2 \ddot{\beta}^2 \sin^2 \alpha) + \frac{1}{2} I_x (\dot{\phi} \sin \theta \cos \phi - \dot{\theta} \sin \phi)^2 + \frac{1}{2} I_y (\dot{\phi} \sin \theta \sin \phi - \dot{\theta} \cos \phi)^2 + \frac{1}{2} I_z (\dot{\phi} \cos \theta)^2 + V(R, \gamma, \xi)
\]
where \( \gamma \) is the angle between \( R \) and the body fixed \( z \) axis and \( \xi \) is the angle between \( R \) and the body fixed \( x \) axis. Therefore
\[
\cos \gamma = \cos \theta \cos \alpha + \sin \theta \sin \alpha \sin(\phi - \beta),
\]
\[
\cos \xi = \sin \theta [\cos \alpha \sin \theta - \cos \phi \sin(\phi - \beta)] + \cos \theta \sin \alpha \cos(\phi - \beta).
\]
In terms of the canonical momenta \( H \) is
\[
H = \frac{\dot{p}_R^2}{2\mu R^2} + \frac{\dot{p}_\alpha^2}{2\mu R^2 \sin^2 \alpha} + \frac{\dot{p}_\beta^2}{2\mu R^2 \sin^2 \alpha \sin^2 \beta} + \frac{A}{2} \left( \frac{\dot{\phi}}{\sin \theta} + \rho_\phi \cos \theta \frac{\dot{\phi}}{\sin \theta} \right)^2 + \frac{B}{2} \left( \frac{\dot{\phi}}{\sin \theta} - \rho_\phi \sin \theta \frac{\dot{\phi}}{\sin \theta} \right)^2 + \frac{C \phi^2}{2} + V(R, \gamma, \xi),
\]
where \( p_R, p_\alpha, p_\beta \) are as in Appendix A and
\[
p_R = \mu \dot{R}, \quad p_\alpha = \mu \dot{R} \alpha, \quad p_\beta = \mu R \dot{\beta} \sin \alpha \beta.
\]
(Note that \( \mu \) is the reduced mass of the "two-body" system, where one body is the atom and the other is the rotor.) Since \( \phi \) and \( \beta \) only occur in the combination \( (\phi - \beta) \), \( \phi \) can be replaced by the new variable \( \epsilon = (\phi - \beta) \). This is done by the \( F_3 \) generator
\[
F_3(\phi, \beta; \epsilon, \beta) = -\beta p_\beta - \epsilon p_\epsilon,
\]
which gives the new momenta \( p_\epsilon = p_\beta = m \) and \( M = p_\phi + \rho_\phi \), the projection of the total angular momentum on the space-fixed \( z \) axis. The orbital angular momentum \( L \) is now introduced by an \( F_3 \) type generator using
\[
L = \frac{p_\phi^2}{2\mu R^2} + \frac{(M-m)^2}{2\mu R^2 \sin^2 \alpha},
\]
\[
F_3(\epsilon, \beta, \alpha; l, m, M) = m \epsilon + \beta M + l \cos \epsilon \left( \frac{l \cos \alpha}{(l^2-(M-m)^2)^{1/2}} \right) - (M-m) \cos \epsilon \left( \frac{(M-m) \cos \alpha}{\sin \alpha (l^2-(M-m)^2)^{1/2}} \right)
\]
The new coordinates are
\[
q_1 = \cos \epsilon \left( \frac{l \cos \alpha}{(l^2-(M-m)^2)^{1/2}} \right),
\]
\[
q_2 = \beta - \cos \epsilon \left( \frac{(M-m) \cos \alpha}{\sin \alpha (l^2-(M-m)^2)^{1/2}} \right),
\]
where \( M = m \), \( L_z = -(M-m) \cos \alpha \), \( L_x = -\cos \epsilon q_2 (l^2-(M-m)^2)^{1/2} \), \( L_y = -\sin \epsilon q_2 (l^2-(M-m)^2)^{1/2} \), \( J_z = J \), so that the magnitude of the total angular momentum \( J \) is given by
\[
J^2 = q_1^2 + q_2^2 + 2m(M-m)
\]
J. Chem. Phys., Vol. 61, No. 8, 15 October 1974
It is now desired to replace \( m \) by \( J_i \) and to express \( \psi \) and
\[
F_4(j, l, M, m; J_i, j, l, M) = J \sin^\star \left( \frac{(M^2 + j^2 - l^2) - 2Mj^2}{\xi (j^2 - m^2)} \right) + l \sin^\star \left( \frac{(M^2 + l^2 - j^2) - 2Ml^2}{\xi (l^2 - m^2)} \right) + j \sin^\star \left( \frac{(M^2 + j^2 - l^2) - 2Mj^2}{\xi (j^2 - m^2)} \right) + M \sin^\star \left( \frac{(j^2 + l^2 - M^2) - 2Mj^2}{2(j^2 - m^2)} \right)
\]

where \( \xi \equiv -J^4 - j^4 - l^4 + 2J^2j^2 + 2J^2l^2 + 2j^2l^2 \).

The new coordinates are
\[
q_j = q_j^1 + \sin^\star \left( \frac{(M^2 + j^2 - l^2) - 2Mj^2}{\xi (j^2 - m^2)} \right)
q_l = q_l^1 + \sin^\star \left( \frac{(M^2 + j^2 - l^2) - M(j^2 - l^2 - j^2)}{\xi (j^2 - m^2)} \right),
q_j = q_j^1 + \sin^\star \left( \frac{(j^2 + l^2 - M^2) - 2Mj^2}{2(j^2 - m^2)} \right)
q_l = q_l^1 + \sin^\star \left( \frac{(j^2 + l^2 - M^2) - 2Ml^2}{2(j^2 - m^2)} \right).
\]

Because of the over-all 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
\[
cos \gamma = \frac{q_j^1 - q_l^1}{l} \left( \cos q_1 \cos q_j + \frac{J^2 - j^2 - l^2}{2l} \sin q_1 \sin q_j \right) + \frac{q_l^1 \sin q_1}{2l} \sin q_j,
\]

The Hamiltonian is now given by
\[
H = \frac{p_j^2}{2 \mu_j} + \frac{p_l^2}{2 \mu_l} + \frac{j^2}{2}(A \sin^2 q_4 + B \cos^2 q_4) + k^2(C - A \sin^2 q_4 - B \cos^2 q_4) + V(R, \gamma, \xi).
\]

APPENDIX C: MONTE-CARLO TECHNIQUE FOR ASYMMETRIC ROTOR TRANSITIONS

Principally because the second "quantum number" \( \nu \) 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
\[
\sigma_{\nu \nu} = \frac{\pi \hbar^2}{(2 \mu E)(2 \tilde{J}_i + 1)} \sum_{j, l} (2J + 1) \sum_{j, l} \left| S^j_{i, j, l, j, l, j, l} \right|^2,
\]

where
\[
S^j_{i, j, l, j, l, j, l}(E) = \left( \frac{2\pi i \hbar}{\delta(q_{1}, q_{1}, q_{1}, q_{1})} \right)^{1/2} e^{i \theta_{q_{1}, q_{1}, q_{1}, q_{1}} / \delta(q_{1}, q_{1}, q_{1}, q_{1})}.
\]

Equation (C1) is transformed to a form suitable for Monte-Carlo evaluation by ignoring the phase in (C2) and averaging over final quantum numbers so that the Jacobian factor in (C2) cancels out.

We first approximate the infinite sum over \( \tilde{J}_i \) by an integral over \( \tilde{J}_i \). If this integral is then transformed into an integral over \( \delta q \), the factor \( \delta \tilde{J}_i / \delta q_i \) which arises cancels with the Jacobian in the S-matrix element. We now have
\[
\sigma_{\nu \nu} = \frac{\pi \hbar^2}{(2 \mu E)(2 \tilde{J}_i + 1)} \sum_{j, l} (2J + 1) \sum_{j, l} \left| S^j_{i, j, l, j, l, j, l} \right|^2
\]

To completely remove the Jacobian we want to average \( j \) and \( \nu \) over "quantum number" intervals. This is straightforward for \( j \) but not for \( \nu \) since this is not an integer for the desired final state and may be imaginary. Because of this last difficulty we average over a \( \nu^2 \) interval rather than a \( \nu^2 \) interval and take the averages of the \( \nu^2 \) values for the various states as the endpoints. We now have
\[
\frac{\delta q_{1}}{\delta q_{1}} = \frac{1}{2\pi i} \int d(\delta q_{1}) \left( \frac{1}{(2\pi \hbar)^{1/2}} \right)^{1/2} e^{i \theta_{q_{1}, q_{1}, q_{1}, q_{1}} / \delta(q_{1}, q_{1}, q_{1}, q_{1})}.
\]

Since it is more convenient to compute the trajectories in the \( k, q_k \) set of canonical variables rather than the \( \nu, \nu \) set, we would like the expression to involve only the former set. The results in Appendix A we have that
\[
\frac{\delta q_{4}}{\delta q_{4}} = (1 + \kappa) + (1 - \kappa) \sin^2 q_4 \left[ (\nu_j^2 + j_j + 1) (\nu_j + 1) \sin^2 q_4 \right]^{1/2}
\]
so that

$$\int d(\nu_2^2) = 2\nu_2 \int d\nu_2 = 2\nu_2 \int \frac{3\nu_2}{\nu_1} \frac{d\nu_1}{d\nu_2} = 2\nu_2 \int \frac{3\nu_2}{\nu_1} \frac{d\nu_1}{d\nu_2} \frac{d\nu_1}{d\nu_2}.$$

If we insert a function \( \chi \) that is one if a trajectory falls in the appropriate \( j_2, \nu_2^2 \) "box" and zero otherwise we get finally

$$o_{j_2, \nu_2^2- j_1} (\nu_1^2) = \frac{\pi R^2 \nu_1^2}{2 \mu E (2j_1 + 1) \Delta} \sum_{j_2} \frac{1}{2j_1 + 1} \int_{j_2 - j_1}^{j_2 + j_1} \int_{j_2 - j_1}^{j_2 + j_1} \int_{j_2 - j_1}^{j_2 + j_1} d\theta d\phi d\psi \left( \frac{\nu_2}{\nu_1} \right) \chi \frac{\nu_2}{\nu_1} \frac{d\theta}{2\pi} \frac{d\phi}{2\pi} \frac{d\psi}{2\pi} \right)^{1/2} \left( \nu_2^2 (1 + \kappa) + (1 - \kappa) \sin^2 \theta \right)^{1/2} \left( \nu_1^2 + j_1 (j_1 + 1) (1 - \kappa) \sin^2 \theta \right)^{1/2}.$$

(C6)

where \( \Delta \) is the length of the \( \nu_2^2 \) "box." Equation (C6) is now in a form amenable to Monte-Carlo evaluation and is the desired result.

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