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Bimolecular Recombination Reactions: Low Pressure Rates in Terms of Time-Dependent Survival Probabilities, Total *J* Phase Space Sampling of Trajectories, and Comparison with RRKM Theory

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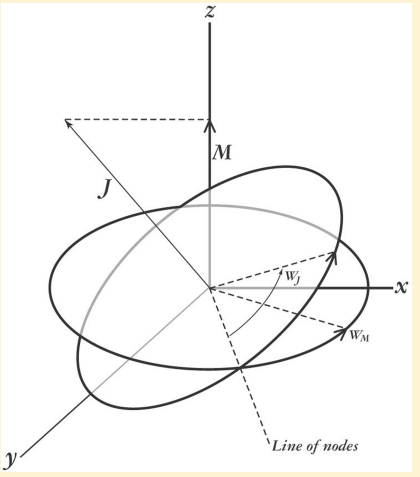
ABSTRACT: We consider the bimolecular formation and redissociation of complexes using classical trajectories and the survival probability distribution function $P(E,J,t)$ of the intermediate complexes at time t as a function of the energy E and total angular momentum quantum number J. The $P(E,J,t)$ and its deviation from single exponential behavior is a main focus of the present set of studies. Together with weak deactivating collisions, the $P(E,J,t)$ and a cumulative reaction probability at the given E and J can also be used to obtain the recombination rate constant k at low pressures of third bodies. Both classical and quantum expressions are given for k in terms of $P(E,J,t)$. The initial conditions for the classical trajectories are sampled for atom−diatom reactions for various (E,J)'s using action-angle variables. A canonical transformation to a total J representation reduces the sampling space by permitting analytic integration over several of the variables. A similar remark applies for the calculation of the density of states of the intermediate complex ρ and for the number of states N^* of the transition state as a function of E and J. The present approach complements the usual approach based on the rate of the reverse reaction, unimolecular dissociation, and the equilibrium constant. It provides results not necessarily accessible from the unimolecular studies. The formalism is applied elsewhere to the study of nonstatistical aspects of the recombination and redissociation of the resulting ozone molecules and comparison with RRKM theory.



1. INTRODUCTION

The formation and dissociation of vibrationally hot molecules has been the subject of numerous studies of bimolecular recombination and unimolecular dissociation chemical reaction rates.[1] Of particular interest has been the validity and the limitations of a statistical theory of these reactions, a theory that assumes that all vibrational−rotational quantum states (or classically all vibrational−rotational phase space) of the molecule at a given energy E and total angular momentum quantum number J are equally accessible by the long-lived vibrationally excited species. In the latter, some qualification on K, the z-component of J with the smallest moment of inertia ("adiabatic" or "active"),[2] is often invoked.

There are many calculations of unimolecular[3−9] and bimolecular[10−12] reaction rates using classical trajectories. These results have been compared with experimental data on the rates of these reactions, usually in the gas phase. Using a sampling of the trajectories appropriate to the experiments, the bimolecular results have also been used to compare with differential and total reaction cross sections studied in molecular beam and other experiments.[13−18]

In the case of unimolecular reactions, a microcanonical ensemble of systems is usually[19−22] considered for different E and J. The corresponding E- and J-dependent rate constant $k(E,J)$ is then determined and introduced into a master equation for the pressure-dependent unimolecular rate constant at the given temperature T.

Most classical trajectory studies of unimolecular dissociation and bimolecular recombination reactions have been made on the former. In a sense, studies of dissociation and recombination are complementary. When the vibrational/rotational relaxation is faster than the reaction rate, the recombination rate constant can be obtained from the dissociation rate constant and the equilibrium constant using detailed balance.[23] However, under other conditions, this need not be the case. There is another aspect in which the unimolecular dissociation and the reverse reaction of a bimolecular recombination differ, namely, in the depletion of the state population at low pressures, described later.

More generally, if the results were reported as a function of each initially sampled part of phase space and to each sampled part of the final phase space, very detailed information from one could be used to obtain equally detailed information on the reverse process (microscopic reversibility). However, just as time-resolved and spectrally resolved studies are typically complementary due to incomplete information, the same is expected for recombination and dissociation processes.

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In the present work, we set up expressions for the trajectory studies for the recombinations, $A + BC \rightarrow ABC^* \rightarrow AB + C$ and $A + BC \rightarrow ABC^* \rightarrow A + BC$, at low third-body pressures. The results can be compared with RRKM theory, and non-RRKM effects can be examined. Weak collision models are used for stabilization of the vibrationally excited intermediates. The focus is on the time-dependent survival probability $P(E,J,t)$ of the energetic intermediate and what can be learned from it in terms of nonstatistical effects.

In the present treatment of a bimolecular collision of an atom and a diatomic molecule that forms an intermediate and then later dissociates or is collisionally deactivated, the overall reaction rate constant is obtained from the rate of formation of the intermediate complexes, together with $P(E,J,t)$, and the rate of stabilizing collisions. A deviation of the collision-free survival probability from a single exponential decay in time for a given E and J provides information on one type of nonstatistical ("non-RRKM")[2] behavior. Even in the single exponential case, a deviation between its decay rate constant and the RRKM value can provide information on another non-RRKM effect, namely, if some of the triatomic phase space is completely inaccessible to the entrance channels.

There are various ways of selecting the initial conditions for bimolecular reactions in the relevant ensemble. We use a method that utilizes action-angle variables. They have been used previously for treating collisions with rotational−translational energy transfer[24,25] and in the semiclassical theory of reactive and nonreactive collisions.[26−29] In exploring directly any nonstatistical behavior, the collisions of the two reactants are studied as a function of E and J.

In practice, the selection of the initial variables in a microcanonical ensemble can be made in various equivalent ways.[19] In one method, the phase space is selected such that the system lies in a certain range, $(J, J + dJ; E, E + dE)$,[3,5,30−32] and sampled. When divided by $dJdE$, one obtains a density in (J,E) space. A second method involves the introduction of delta functions, $\delta(E - E')$ and $\delta(J - J')$, in the integrand.[33−37] A third method, introduced below, involves a canonical transformation to a total J representation and a symmetry-based analytic integration over several of the variables. For comparison, we give in Appendix B a delta function method that results in conditional probabilities in the form of a Jacobian. It also provides an independent numerical check for computing the various properties. The three methods can be expected to yield equivalent results. For each trajectory, the initial conditions are sampled at a large separation distance where the interaction energy is negligible.

As noted earlier, the main focus of the present work is on the time-dependent survival probability $P(E,J,t)$ of the long-lived intermediate in a bimolecular recombination, its deviation from single exponential decay, what it reveals about differences in the dynamics of the two exit channels, and its comparison with statistical theory. The paper is organized as follows. In section 2, a classical expression for the recombination rate constant is given in the total J-representation, containing a cumulative reaction flux term $W(E,J)$ for forming an intermediate and $P(E,J,t)$, both based upon classical trajectories. The phase space sampling of trajectories of the bimolecular collisions is also given there using action-angle and other phase space variables. The initialization of the usual Cartesian and momentum coordinates of the atom−diatom system for the trajectories is given in terms of these action-angle variables in Appendix A. In section 3, a formal quantum version of the low pressure recombination rate constant and $P(E,J,t)$ using wavepackets is given for a comparison with the classical results. In section 4, the density of states of the energetic intermediate and the number of states at the transition state are discussed and an expression is given for the recombination rate constant at low pressures. The results are summarized in section 5, together with concluding remarks. Specific applications of the classical expressions will be given elsewhere.

2. BIMOLECULAR TRAJECTORIES LEADING TO COLLISION COMPLEXES: CLASSICAL RATE CONSTANT AND PHASE SPACE SAMPLING

Almost all trajectory studies of long-lived intermediates are made via the study of the dissociation, and an equilibrium constant is used to obtain the bimolecular recombination rate constant. Nevertheless, not all features of the recombination are captured in this way. For example, in an atom−diatom collision such as $A_1 + BA_2 \rightarrow A_1BA_2$, where A_1 and A_2 are identical, one would not see in a unimolecular study any propensity for the newly formed bond A_1B to dissociate more readily than A_2B. However, it is immediately apparent, we found, in a bimolecular study. There is another difference. For the recombination rate constant in the limiting low pressure region, there are two zeroth-order processes, the formation of the vibrationally excited intermediate from the collision of the two reactants and the redissociation of that intermediate prior to any collision with a third body. The next-order processes are, instead, the collisions that change the energy of this intermediate. Because the zeroth-order processes dominate at low pressures, the population of the energetic intermediate is in equilibrium with the reacting pair for the dynamically accessible domain at the given energy in zeroth order. On the other hand, for the unimolecular dissociation process, the dominant steady-state terms at low pressures involve energy transfer collisions, one of them leading to dissociation. Thus, now a depletion appears in the steady-state expression for the phase-space-dependent dissociating population in the low pressure limit of the unimolecular dissociation rate constant and has to be included.[38,39] In this respect, the study of the dissociation and recombination reactions can again differ.

In the present work, the initial conditions are selected using action-angle variables. For simplicity of notation, the action variables will be given in units of h, and thus they also represent quantum numbers. The variables for the atom−diatom system consist of the action variable j for the angular momentum of the diatom $j/2\pi$, the z-component m_j along a space-fixed z-axis, the action-variable l for the orbital angular momentum $l/2\pi$ of the two colliding partners, the z-component m_l, and the action n for the vibration of the diatom. The angle variables canonically conjugate to j, l, m_j, m_l, and n are denoted by w's. In the center-of-mass system of coordinates, the remaining momentum of the six momenta is P_R, the momentum conjugate to the center-to-center separation distance R of the colliding reactants. These variables and the associated incident flux term for the phase space of the atom−diatom system are chosen for both the microcanonical and canonical systems. Because the action variables are written here in units of h, a canonically conjugate action-angle pair such as j and w_j that would normally have a phase space volume element $dj dw_j/h$ as dimensionless now has $dj dw_j$ as dimensionless.

For setting up a classical trajectory study for a bimolecular recombination rate constant in terms of the time-dependent survival probability, the low pressure third-order rate constant for an atom−diatom system is given by eq 1 for the case of a weak

deactivating collision:

$$k = \frac{1}{h}\int \cdots \int P(E,\Gamma_{10},t)Z(E',E)\Theta_c(E,\Gamma_{10})e^{-E/kT}\frac{dEdE'd\Gamma_{10}dt}{Q_{elec}Q_{trans}Q_{rot-vib}} \quad (1)$$

where the step function $\Theta_c(E,\Gamma_{10})$ is 1 or 0 according to whether an intermediate is or is not formed from the trajectory of the colliding partners, $P(E,\Gamma_{10},t)$ is the survival probability for the intermediate complex at time t, and Q_{elec}, Q_{trans}, and $Q_{rot-vib}$ are the electronic, translational (per unit concentration) in the center-of-mass system of coordinates, and the rotational−vibrational partition functions of the colliding partners.[40] $d\Gamma_{10}$ denotes $dld m_l dj dm_j dn dw_l dw_{m_l} dw_j dw_{m_j} dw_n$. The limits for the multiple integrals are $(-l,l)$ for m_l, $(-j,j)$ for m_j, $(0,1)$ for the w's, $(0,\infty)$ for E, l, j, n, and t, and, for a successful "three-body collision", $(-D,0)$ for E'. Here, D is the dissociation energy of the triatomic species and 0 is the energy of the potential energy asymptote at large separation distances of the two reactants. The dE in eq 1 arises from the expression for the incident flux in the customary way: the number of quantum states $dRdP_R/h$ occupying a phase space volume element $dRdP_R$ is divided by dR to yield an incident probability density per unit R and then multiplied by a velocity $\dot{R}$ to yield for the flux $\dot{R}dP_R/h$. The latter equals $d(P_R{}^2/2\mu)/h = dE_{trans}/h = dE/h$ at a fixed value of the other variables. Here, μ is the reduced mass of the atom−diatom collision partners.

The $1/h$ in eq 1 and the $1/h^5$ tacitly present in $d\Gamma_{10}$ cancel the $1/h^6$ present in the $Q_{trans}Q_{rot-vib}$, so that eq 1 for the classical observable k is independent of h. Equation 1 applies to the case where all electronic states but the lowest one are too shallow to contribute to the overall recombination rate constant.

The $Z(E',E)\,dE'$ in eq 1 is the number of collisions per unit volume per unit time that lead to an energy transfer for the vibrationally excited intermediate from E to $(E',E'+dE')$. It is proportional to the concentration M of third-bodies, and the three-body low pressure order rate constant k in eq 1 has units of $cm^6/molecule^2/s$. Strictly speaking, instead of $Z(E',E)$ we have $Z(E'J',EJ)$ for a transition $(JE)\rightarrow(J'E')$ in a collision when J is the total angular momentum quantum number of the vibrationally excited intermediate. However, if for simplicity of presentation we assume that J has a thermal distribution after a collision then $Z(E'J',EJ) = P(J')Z(E',E)$ independently of J,[1c,41] where $P(J')$ is the thermal equilibrium distribution of J' at the given temperature. Eventually, the sum over all J' yields unity and what remains is given by eq 1. It is useful to note therefore that in this formulation $E'-E$ is the total energy transfer, not just the vibrational energy transfer. When the deactivating collisions are weak, a property typically assumed now in dissociation and recombination reactions[41−45] and supported by experiment,[38,46,47] the collision frequency $Z(E',E)$, is that for a weak collision. Models for the collision energy transfer property $Z(E',E)$ include the stepladder,[42,43,48,49] single exponential,[38,39,42] biexponential,[39,50,51] singularity,[39] and near singularity[39] models.

In using eq 1, the time t that each classical trajectory, specified by its values of E and Γ_{10}, exists as an energetic intermediate is noted. For that value of E and Γ_{10}, $P(E,\Gamma_{10},t)$ equals unity for the trajectory for times less than this time t and zero thereafter.

To implement eq 1 and study the time-dependent survival probability of the energetic intermediate as a function of E and J, the total angular momentum quantum number, it is convenient to introduce a canonical transformation from the variables in Γ_{10} to a total J representation with variables that include J and its space-fixed z-component M:

$$jlm_jm_lnw_jw_lw_{mj}w_{ml}w_n \rightarrow jlJMnw_jw_lw_Jw_Mw_n$$

One can also include P_R and R in both sides and so make a canonical transformation of all the variables.

A formal generating function for the transformation has been given,[29] but for our purpose, it suffices to know that the Jacobian of a canonical transformation is unity. We denote the new variables $jlJMnw_jw_lw_Jw_Mw_n$ by Γ^J_{10}, and thus write $d\Gamma^J_{10} \equiv dJd\Gamma_9$ and $d\Gamma_9 \equiv djdldMdndw_jdw_ldw_Jdw_Mdw_n$.

In terms of Γ^J_{10}, we can write instead of eq 1 an equally valid expression for the rate constant k

$$k = \frac{1}{h}\int \cdots \int P(E,\Gamma^J_{10},t)Z(E',E)\Theta_c(E,\Gamma^J_{10})e^{-E/kT}\frac{dEdE'd\Gamma^J_{10}dt}{Q_{elec}Q_{trans}Q_{rot-vib}} \quad (2)$$

We have used the fact that the Jacobian of the transformations from Γ_{10} to Γ^J_{10} is unity.

Equations 1 and 2 involve a detailed tracking of each trajectory in (E,Γ_{10}) or (E,Γ^J_{10}) space, respectively. However, this information is for typical purposes excess information and it is useful to count instead the number of intermediate complexes formed at $t = 0$ at a given E and J and the fraction of those that survive at any time t. We thereby introduce a time-dependent survival probability $P(E,J,t)$ for systems at a given E and J that is the fraction of intermediate complexes formed at $t = 0$ that has survived at time t:

$$P(E,J,t) = \frac{\int \cdots \int P(E,\Gamma^J_{10},t)\Theta_c(E,\Gamma^J_{10})\,d\Gamma_9}{\int \cdots \int \Theta_c(E,\Gamma^J_{10})\,d\Gamma_9} \quad (3)$$

where $P(E,J,t)$, a dimensionless quantity, equals unity at $t = 0$. Since the integration in eq 3 is over Γ^J_9 while the integral is a function of Γ^J_{10}, this P is a function of J. It permits a direct and detailed comparison with the result for RRKM theory for various E and J.

We denote the denominator in eq 3 by $W(E,J)$, a dimensionless term related to the incident flux, which serves as a cumulative reaction term in (E,J) space:

$$W(E,J) = \int \cdots \int \Theta_c(E,\Gamma^J_{10})\,d\Gamma_9 \quad (4)$$

Thereby, eq 2 can be written as

$$k = \frac{1}{h}\int \cdots \int P(E,J,t)W(E,J)Z(E',E)e^{-E/kT}\frac{dJdEdE'dt}{Q_{elec}Q_{trans}Q_{rot-vib}} \quad (5)$$

where the limits are $(0,J_{max})$ for J and the limits given earlier for the remaining variables. This equation has been written in a form that parses k into the different contributions from the various E's and J's. In eq 5, as already noted, $P(E,J,t)$ and $W(E,J)$ are dimensionless, $Z(E',E)\,dE'$ has units of $cm^3/molecule/s$, Q_{elec} and $Q_{rot-vib}$ are dimensionless, $1/Q_{trans}$ has units of $cm^3/molecule$, and $dEdt/h$ is dimensionless. Thus, k has units of $cm^6/molecules^2/s$, the units of a three-body recombination reaction rate constant.

Equations 3 and 4 can be simplified further. We consider first a fixed M, the space-fixed z-component of the total angular

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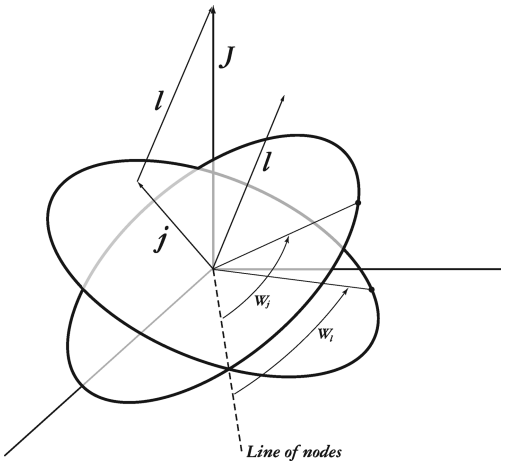

Figure 1. Variables in the reduced rotational−orbital space, depicting the various action angle variables.

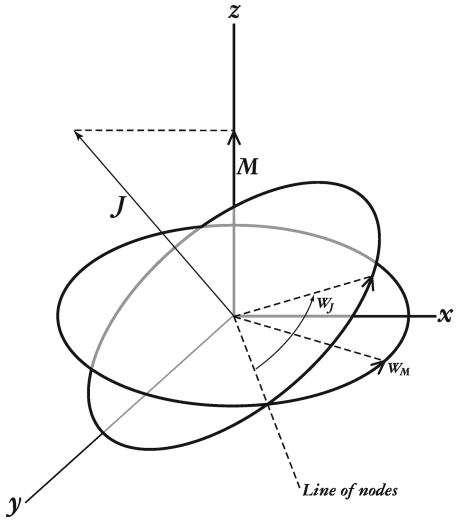

Figure 2. Planes describing the variables w_j and w_M canonically conjugate to J and M.

momentum quantum number J, and a fixed w_M and w_J, the angle variables conjugate to J and M. Each integral in eqs 3 and 4 over the remaining variables is, one can see on physical grounds, independent of these three variables and so we can immediately integrate over M, w_M, and w_J, yielding values of $2J$, 1, and 1. Equations 3 and 4 now become

$$P(E,J,t) = \frac{\int \cdots \int P(E,\Gamma_6,t)\Theta_c(E,\Gamma_6)\, d\Gamma_6}{\int \cdots \int \Theta_c(E,\Gamma_6)\, d\Gamma_6} \quad (6)$$

$$W(E,J) = 2J \int \cdots \int \Theta_c(E,\Gamma_6)\, d\Gamma_6 \quad (7)$$

where $\Gamma_6 \equiv (j,l,n,w_j,w_l,w_n)$. The rotational−orbital variables are depicted in Figure 1, where we have placed the vector corresponding to J along the z-axis. The planes of motion describing J, M, w_M, and w_J are depicted in Figure 2. The

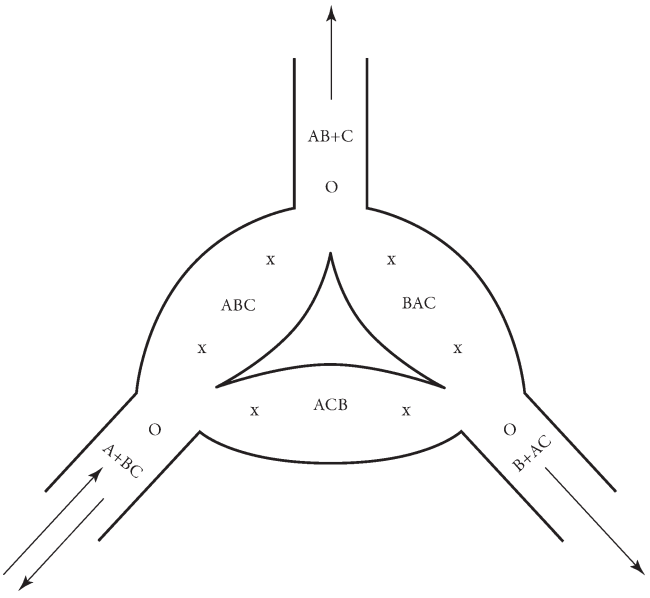

Figure 3. Schematic illustration of "phase space" and reaction pathways for a general atom−diatom collision, A + BC → ABC* → products. The loose (O) and tight (X) transition states are marked.

relation of the conventional Cartesian coordinates and momenta to the variables in Figure 1 is given in Appendix A.

There is an additional aspect to be considered in a collision A + BC. The high energy intermediate can dissociate either via the channel from which it came or via the other channel. This factor enters into any comparison with RRKM theory. The collision A + BC can form ABC or ACB. Considering the former first, we distinguish two sets of reaction products after the formation of an intermediate ABC, A + BC, and AB + C. For analyzing any nonstatistical effect, $P(E,\Gamma_6,t)$ is decomposed into the contribution from those $P_{en}(E,\Gamma_6,t)$ that at time t later dissociate into the entrance channel (A + BC) and those $P_{ex}(E,\Gamma_6,t)$ that dissociate into the second channel (AB + C) (ex for exchange). In the comparison, one also has to distinguish the trajectories that form ABC from those that form ACB, as in Figure 3, where the different regions and the "loose" and "tight" transition states (TS) are depicted schematically. In a loose TS, the two reactants rotate freely, and in a tight TS, they do not. The actual situation is typically somewhere in between.

3. QUANTUM VERSION OF RECOMBINATION RATE CONSTANT AT LOW PRESSURES

In a quantum version of eq 1, a direct analogue would be the use of a wavepacket containing wave functions of a particular (j,l,m_j,m_l,n) or (j,l,J,M,n) with a small range ΔE of translational energies for the colliding particles. The desired width ΔE of the packet is such that its Δt counterpart, $h/\Delta E$, is small relative to the lifetimes of interest. For example, in the low pressure region, if the pressure of third bodies is of the order of 1 atm at 298 K, the average time between collisions for deactivation of an energetic ozone intermediate with a third body, such as N_2, is about 200 ps. If ΔE were selected to be about 0.25 kT, i.e., about 50 cm^{-1} at room temperature, then the time resolution would be of the order of 1 ps.

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For k, we write

$$k = \int\int\int \sum_{\Gamma} P(\Gamma_S, v, t) v \sigma(\Gamma_S, v) Z(E', E) v^2 e^{-E/kT} \frac{dE' dv dt}{Q_{elec} Q_{rot-vib} I_v} \quad (8)$$

where Γ_S now denotes quantum state numbers (j,l,m_j,m_l,n) and v is the mean velocity of the wavepacket, $\sigma(\Gamma_S,v)$ is the total reactive scattering cross section, $P(\Gamma_S,v,t)$ denotes the survival probability that a complex formed from state Γ_S and v survives at time t, and I_v is the integral $I_v = \int_0^\infty v^2 e^{-\mu v^2/2kT} dv = (\pi/2)^{1/2} (kT/\mu)^{3/2}$. In eq 8, we note that v^2 is related to E, j, and n in Γ_S by

$$v^2 = 2[E - H_0(j,n)]/\mu \quad (9)$$

where $H_0(j,n)$ is the initial rotational−vibrational energy of the diatomic molecule.

When comparing with RRKM theory at a given E and J, it is convenient to introduce an E- and J-dependent cross section $\sigma(\Gamma_J,v)$, using Clebsch−Gordan coefficients. That is, the Clebsch−Gordan coefficients are implicitly included in this $\sigma(\Gamma_J,v)$. We then have for the rate constant

$$k = \int\int\int \sum_{J} P(E,J,t) W(E,J) Z(E', E) e^{-E/kT} \frac{dE' dv dt}{Q_{elec} Q_{rot-vib}} \quad (10)$$

where

$$W(E,J) = \sum_{\Gamma_J} v^3 \sigma(\Gamma_J, v)/I_v \quad (11)$$

and

$$P(E,J,t) = \frac{\sum_{\Gamma_J} P(\Gamma_J, v, t) v^3 \sigma(\Gamma_J, v)}{\sum_{\Gamma_J} v^3 \sigma(\Gamma_J, v)} \quad (12)$$

Here, Γ_J denotes collectively the five quantum numbers (J,M,j,l,n). The $\sigma(\Gamma_J,v)$ tacitly includes the Clebsch−Gordan coefficients in its definition, and the sum is over Γ_J, with an accompanying choice of v that satisfies the energy condition given in eq 9. The integration or summation limits in eq 10 for E', J, and t are the same as before, and the integration over v is from 0 to ∞. In eq 10, $W(E,J)\,dv$ has units of cm^3/molecule, $Z(E',E)\,dE'$ again has units of cm^3/molecule/s, and k has units of cm^6/molecule^2/s.

4. CALCULATION OF RECOMBINATION RATE CONSTANT FROM RRKM LIFETIME DISTRIBUTION

i. RRKM, Lifetime Distribution for Comparison with Classical Trajectory Results. In eqs 1, 2, and 5, the time-dependent survival probability of the intermediate in the recombination rate constant was based on trajectories. In this section, we consider the recombination rate constant based on the survival probability $P_{RRKM}(E,J,t)$ for a statistical (RRKM) theory. The comparison between these two $P(E,J,t)$'s permits the identification of non-statistical contributions to the rate.

In the classical limit of the RRKM expression, $k_{RRKM} = N^*(E,J)/h\rho(E,J)$ for a vibrationally excited molecule with s coordinates; $N^*(E,J)$ and $N^*(E,J)h^{s-1}$ are, respectively, the number of quantum states and the volume of phase space occupied by a transition state with rovibrational energy equal to or less than E at a given quantum number J (per unit J). The $\rho(E,J)h^s$ is the volume of phase space per unit energy and per unit J occupied by the energetic molecule for the given J. The powers of h cancel in the classical limit for $k_{RRKM}(E,J)$, as they should.

In the case of RRKM theory, we have

$$P_{RRKM}(E,J,t) = e^{-k_{RRKM} t} \quad (13)$$

for a triatomic intermediate, and the step function $\Theta_c = 1$ if $N^*(E,J) \geq 0$ and 0 otherwise. For this purpose, eq 1 for the low pressure three-body recombination rate constant is replaced by

$$k = \frac{1}{h}\int\int\int\int P_{RRKM}(E,J,t) Z(E',E) \Theta_c(E,J) e^{-E/kT} \frac{N^*(E,J)\, dJ dE dE' dt}{Q_{elec} Q_{trans} Q_{rot-vib}} \quad (14)$$

The step function $\Theta_c(E,J)$ in eq 14 is not redundant. Although this information is contained in $N^*(E,J)$, the N^* will later cancel an N^* in P_{RRKM} after the integration over t, but the information of whether or not the collision leads to a vibrationally excited intermediate does not cancel. A comparison of eqs 5 and 14 reveals that the transition state equivalent of $W(E,J)$ is $\Theta_c(E,J)N^*(E,J)$.

The integration in eq 14 over t yields

$$k = \int\int\int \rho(E,J) Z(E',E) \Theta_c(E,J) e^{-E/kT} \frac{dE dE' dJ}{Q_{elec} Q_{trans} Q_{rot-vib}} \quad (15)$$

The $1/h^6$ in $\rho(E,J)$ cancels the $1/h^3$ from $Q_{rot-vib}$ and the $1/h^3$ from Q_{trans}. The classical result is seen to be independent of h, as it should be. The limits of integration in eqs 14 and 15 are the same as before.

For the quantum version of eq 15, one merely uses the quantum version of $\rho(E,J)$, now the density of states for a given J, and uses the quantum version of $Q_{rot-vib}$, and requires that $\Theta_c(E,J) = 1$ when $N^*(E,J) \geq 2J+1$.

ii. Classical Density of States for RRKM Theory in the Recombination Rate Constant. We consider the density of states $\rho(E,J)$ for the triatomic system for a given total angular momentum quantum number J and energy E. We use variables appropriate to an atom−diatom system. In particular, we use rotational/orbital action-angle variables used in the selection of the initial conditions, together with p_r, r, P_R, and R (P_R is later subsumed in the constant E condition). By not using the usual body-fixed vibrational−rotational coordinates for the intermediate complex, it obviates the need for introducing Coriolis and other rotation−vibration coupling terms for the long-lived intermediate. On the other hand, care is needed to ensure that the integration is over the phase space occupied by the intermediate.

The density of states ρ (per unit energy for the given J) is given in terms of these coordinates and momenta for an atom−diatom system and then j, l, m_j, and m_l are transformed to j, l, J, and M, as noted earlier. We have

$$\rho(E,J) = \int \cdots \int \delta(E - H)\, d\Gamma_7^J dP_R dR dp_r dr/h^2 \quad (16)$$

where $d\Gamma_7^J = dj dl dM dw_j dw_l dw_J dw_M$ (each action here is again in units of h) and H is the total energy in terms of these variables (including a $P_R^2/2\mu$ term). After integration over all variables but M, w_M, and w_J, the result is again independent of the three variables and thus one can immediately integrate over them, yielding values of $2J$, 1, and 1, respectively. For eq 16, a canonical

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transformation from variables containing m_j and m_l to those containing J and M has a Jacobian of unity, and this fact was used in obtaining eq 16. The transformation yielded a dJ, but we can set dJ = 1 to obtain the density of states per unit J, which also is equivalent to a density of states at the given J.

After integration over M, w_M, and w_J, the $\rho(E,J)$ is given by

$$\rho(E,J) = 2J \int \cdots \int \delta(E-H)\, \mathrm{d}\Gamma_4^J \mathrm{d}P_R \mathrm{d}R \mathrm{d}p_r \mathrm{d}r \qquad (17)$$

where $\mathrm{d}\Gamma_4^J = \mathrm{d}j\mathrm{d}l\mathrm{d}w_j\mathrm{d}w_l$ and the $\delta(E-H)$ can be replaced by $\delta(P_R - P_R')/(\partial H/\partial P_R)$ with $\partial H/\partial P_R = P_R/\mu$.

While the ρ is determined uniquely by the variables specified in eq 17, it is necessary to specify additional variables in order to utilize the expression for the conventional coordinates and momenta given in Appendix A. In particular, we note that if J is placed along the z-axis, as in Figure 1, we have $M = J$. Also, m_j is given by $l^2 = j^2 + J^2 - 2m_jJ$ and m_l equals $J - m_j$.

For the two remaining variables, there are four cases: (1) $w_{m_j} = 0$ and $w_{m_l} = 0$, (2) $w_{m_j} = 1/2$ and $w_{m_l} = 1/2$, (3) $w_{m_j} = 1/2$ and $w_{m_l} = 0$, and (4) $w_{m_j} = 0$ and $w_{m_l} = 1/2$. As seen in eqs A1−A12, the pair (1) and (2) are related by inversion symmetry (when all three atoms are the same isotope), and (3) and (4) are similarly related to each other. Further examination of the angle γ (defined in Appendix C) shows that the members of one pair are geometric isomers of the other pair, one being ABC and the other BAC. The relation,[24] $\cos\gamma = \cos\theta\cos\theta_1 + \sin\theta\sin\theta_1\cos u$, with coordinates defined in Appendix C and related to variables defined in Appendix A, was used to see if γ corresponds to the molecule ABC or ACB. For one isomer of the collision complex, ABC, the angle γ lies in $(0,\pi/2)$, and for the other, ACB, γ lies in $(\pi/2,\pi)$. For the transition state, when it is "tight", the same remarks apply. When it is loose, the angle γ fully occupies the $(0,\pi)$ interval.

iii. Transition State for Recombination: Number of States, *N.** For the transition state for the recombination, two limiting reaction coordinates are sometimes used: (1) R, the distance between the centers of mass of the two colliding reactants, and (2) the distance between the two atoms of the newly forming chemical bond. For a "loose" TS in which AB rotates relatively freely, the former is the natural choice, and for a "tight" TS, the latter is more suitable. A linear combination of them for the microcanonical formalism, given by Klippenstein et al.,[53] gives an improved choice, optimized so as to have the least value of N^* (and thus corresponding to a TS having the fewest recrossings of the TS by trajectories). The role played by the recrossing criterion was noted by Wigner in his classic 1937 paper.[54]

When R can be used as a reaction coordinate, the number of quantum states at the transition state, $N^*(E,J)$, with energy equal to or less than E, denoted by the step function Θ, is given by

$$N^*(E,J) = \min_R \int \cdots \int \Theta(E-H)\, \mathrm{d}\Gamma_7^J \mathrm{d}p_r \mathrm{d}r/h \qquad (18)$$

where $\mathrm{d}\Gamma_7^J$ denotes $\mathrm{d}j\mathrm{d}l\mathrm{d}M\mathrm{d}w_j\mathrm{d}w_l\mathrm{d}w_j\mathrm{d}w_M$, as before. The H is the Hamiltonian at the given R and contains the ${P_R}^2/2\mu$. Once the other coordinates and momenta in H are specified, ${P_R}^2/2\mu$ is given by energy conservation. One also had a dJ but set dJ = 1 as before. Upon integrating over M, w_M, and w_J, $N^*(E,J)$ is then given by

$$N^*(E,J) = \min_R 2J \int \cdots \int \Theta(E-H)\, \mathrm{d}\Gamma_4^J \mathrm{d}p_r \mathrm{d}r/h \qquad (19)$$

where $\mathrm{d}\Gamma_4^J$ again denotes $\mathrm{d}j\mathrm{d}l\mathrm{d}w_j\mathrm{d}w_l$. The N^* in eqs 18 and 19 is determined using variational RRKM theory.[55] Once again, while $N^*(E,J)$ is determined uniquely by the reduced number of variables appearing in eq 19, implementation of the equations for the various coordinates in Appendix A requires the assignment of values for m_j, m_l, w_{m_j}, and w_{m_l}, as discussed for $\rho(E,J)$ in the previous section.

5. SUMMARY AND CONCLUDING REMARKS

Expressions are given for treating the time-dependent survival probability $P(E,J,t)$ and an incident flux cumulative reaction flux term $W(E,J)$ for the intermediate complexes that are formed in atom−diatom collisions. The low pressure recombination rate constant is expressed in terms of these quantities and an energy-dependent collision frequency $Z(E',E)$. A canonical transformation to the total J representation served to simplify the expression by permitting the immediate integration over several variables. The $P(E,J,t)$ and $W(E,J)$ were expressed in terms of classical trajectories, quantum mechanical wavepackets, and, for comparison, RRKM theory. Action-angle variables were used for the sampling of initial conditions for the trajectories and in the calculation of density of states $\rho(E,J)$ and number of states $N^*(E,J)$. Nonstatistical effects in the recombination rate constant calculated by trajectory or wavepackets can be identified in part from the deviation of the survival probability $P(E,J,t)$ from a single exponential.

For a collision, A + BC, the recombination rate constant and the nonstatistical effects for each of the two exit channels from the intermediate complex can be explored. Any of several weak collision models, such as those described in refs 38 and 39, are available for the calculation of the low pressure recombination rate constant. However, the main focus is instead the study of the nonstatistical effects, which can have implications for the quantum analogue. In some alternative approaches, the dissociation behavior has been expressed instead in terms of average state-dependent lifetimes.[12b]

The formalism involving $P(E,J,t)$ is applied elsewhere to the study of nonstatistical aspects of ozone formation by a recombination reaction, and a comparison with RRKM theory. The changes in K, the component of J along the near-symmetric top z-axis of ozone, have been implicated by Schinke and co-workers both in collisional energy transfer of ozone and thereafter intramolecularly into its vibrations.[56,57] A theory of the phenomenon of K diffusion in such near-symmetric top molecules and dissociation, a source of non-RRKM behavior when the diffusion is slow, has recently been given in refs 58 and 59. A detailed discussion of results for RRKM that uses either an adiabatic or an active K for the limiting behavior is given in ref 60.

APPENDIX A: INITIAL CARTESIAN AND MOMENTUM COORDINATES FOR CLASSICAL TRAJECTORIES OF THE ATOM−DIATOM SYSTEM IN TERMS OF ACTION-ANGLE VARIABLES

The initial conditions of interest in phase space for the atom−diatom collision are given here for the action-angle variables and the diatom internuclear distance r, and its conjugate momenta p_r. Specifically, the initial conditions can be chosen for $(j,m_j,l,m_l,n,P_R,w_j,w_{m_j},w_l,w_{m_l},w_n,R)$ for the classical trajectories at an initial center-to-center distance R_i in the noninteraction region. The values for r and p_r are obtained from w_n and n.

In the center-of-mass coordinate system for the collision pair A + BC, we let (Q_1,Q_2,Q_3) denote the Cartesian coordinates of C with respect to B and (Q_4,Q_5,Q_6) to be those of A with respect to the center of mass of the pair (B, C).

The various Cartesian coordinates and their conjugate momenta P's for the atom−diatom system are given in terms of the action-angle variables as follows.[61] (For notational brevity, we write in eqs A1−A12 all of the $2\pi w$'s as w's.)

$$Q_1 = r[\cos w_j \cos w_{m_j} - (m_j/j) \sin w_j \sin w_{m_j}] \quad \text{(A1)}$$

$$Q_2 = r[\cos w_j \sin w_{m_j} + (m_j/j) \sin w_j \cos w_{m_j}] \quad \text{(A2)}$$

$$Q_3 = r[1 - (m_j/j)^2]^{1/2} \sin w_j \quad \text{(A3)}$$

$$P_1 = p_r[-(m_j/j) \sin w_j \sin w_{m_j} + \cos w_j \cos w_{m_j}] - (m_j/r) \cos w_j \sin w_{m_j} - (j/r) \sin w_j \cos w_{m_j} \quad \text{(A4)}$$

$$P_2 = p_r[(m_j/j) \sin w_j \cos w_{m_j} + \cos w_j \sin w_{m_j}] + (m_j/r) \cos w_j \cos w_{m_j} - (j/r) \sin w_j \sin w_{m_j} \quad \text{(A5)}$$

$$P_3 = p_r[1 - (m_j/j)^2]^{1/2} \sin w_j + (j/r)[1 - (m_j/j)^2]^{1/2} \cos w_j \quad \text{(A6)}$$

$$Q_4 = R_i[\cos w_l \cos w_{m_l} - (m_l/l) \sin w_l \sin w_{m_l}] \quad \text{(A7)}$$

$$Q_5 = R_i[\cos w_l \sin w_{m_l} + (m_l/l) \sin w_l \cos w_{m_l}] \quad \text{(A8)}$$

$$Q_6 = R_i[1 - (m_l/l)^2]^{1/2} \sin w_l \quad \text{(A9)}$$

$$P_4 = P_R[-(m_l/l) \sin w_l \sin w_{m_l} + \cos w_l \cos w_{m_l}] - (m_l/R_i) \cos w_l \sin w_{m_l} - (l/R_i) \sin w_l \cos w_{m_l} \quad \text{(A10)}$$

$$P_5 = P_R[(m_l/l) \sin w_l \cos w_{m_l} + \cos w_l \sin w_{m_l}] + (m_l/R_i) \cos w_l \cos w_{m_l} - (l/R_i) \sin w_l \sin w_{m_l} \quad \text{(A11)}$$

$$P_6 = P_R[1 - (m_l/l)^2]^{1/2} \sin w_l + (l/R_i)[1 - (m_l/l)^2]^{1/2} \cos w_l \quad \text{(A12)}$$

The Hamiltonian utilizing eqs A1−A12 can be numerically integrated in a classical trajectory in conventional Cartesian coordinates for a reactive scattering for an atom−diatom system.

When the vector corresponding to J is placed along the space-fixed z-axis, as in Figure 1, these eqs A1−A12 can be simplified: we have $m_j + m_l = J$, and we can select, as in the text for ρ and for N^*, the four cases of the values for w_{m_j} and w_{m_l}, the four pairings of 0 and 1/2 for these variables. In sampling the initial conditions for eqs 6 and 7, the results of a trajectory for these quantities are uniquely defined by the variables Γ_6. We are left with four independent rotational−orbital phase space variables (j, l, w_j, and w_l), in addition to n and w_n. For a given initial R, the initial P_R is determined by j, n, and E. If we place J along the z-axis, as in Figure 1, then $l^2 = j^2 + J^2 - 2m_jJ$, and thus, l can be sampled by sampling m_j in the interval $(-j,j)$. Therefore, in this particular procedure, the sampling variables are j, l (via m_j), w_j, w_l, n, and w_n, while w_{m_j} and w_{m_l} are selected as above, for sampling initial conditions. For sampling for N^*, one would use r and p_r instead. For sampling for ρ, one would add R and P_R to the latter. The m_l is set equal to $J - m_j$ in using eqs A1−A12.

APPENDIX B: SURVIVAL PROBABILITY AND REACTION FLUX WITH DELTA FUNCTIONS

We give here for completeness alternative expressions for $P(E, J,t)$ and $W(E,J)$. With Γ_{10} denoting the variables given in the paragraph following eq 1, we can write the time-dependent survival probability at a given energy E and total angular momentum quantum number J as

$$P(E,J,t) = \frac{\int \cdots \int P(E,\Gamma_{10},t)\Theta_c(E,\Gamma_{10})\delta(J - J')\, d\Gamma_{10}}{\int \cdots \int \Theta_c(E,\Gamma_{10})\delta(J - J')\, d\Gamma_{10}} \quad \text{(B1)}$$

where the $P(E,J,t)$ equals unity at $t = 0$. The J' is expressed in terms of the Γ_{10} variables. The E and the variables in Γ_{10} provide the initial P_R. The $\delta(J - J')$ in eq B1 can be replaced by a $\delta(P - P')/(\partial J'/\partial P)$, where P' is a suitable angular momentum variable in Γ_{10}.

We also introduce a term related to the incident flux $W(E,J)$

$$W(E,J) = \int \cdots \int \Theta_c(E,\Gamma_{10})\delta(J - J')\, d\Gamma_{10} \quad \text{(B2)}$$

The low pressure recombination rate constant k from eq 1 is now again given by eq 5, with $P(E,J,t)$ and $W(E,J)$ now given by eqs B1 and B2.

APPENDIX C: CLASSICAL DENSITY OF STATES FOR RRKM THEORY IN THE RECOMBINATION RATE CONSTANT

We consider the density of states $\rho(E,J)$ at the given J for an atom−diatom complex for a given total angular momentum quantum number J and for a given E, using instead of the variables used in the body of the paper the Jacobi phase space variables. Using Jacobi variables instead of the usual body-fixed vibrational−rotational coordinates for the intermediate complex again obviates the need for introducing Coriolis and other rotation−vibration coupling terms for the long-lived intermediate. In this appendix, the total angular momentum is, reverting to the usual units, $J\hbar$.

In terms of Jacobi coordinates and momenta for an atom−diatom system, we have[34]

$$\rho(E,J) = \frac{1}{h}\int \cdots \int \delta(E - E'')\delta(J - J')\, d\Gamma'_{10} dP_R dR \quad \text{(C1)}$$

where $d\Gamma'_{10} = dP_\theta dP_{\theta_1} dP_\phi dP_{\phi_1} dp_r d\theta d\theta_1 d\phi d\phi_1 dr/h^5$ and E'' is the total energy related to the Jacobi coordinate Hamiltonian (eq C3 below). Here, r, θ, and ϕ are the spherical polar coordinates for the axis of the diatomic rotor, with conjugate momenta p_r, P_θ, and P_ϕ. R, θ_1, and ϕ_1 are the spherical polar coordinates for the vector $\mathbf{R}$ from the atom to the center of mass of the diatom, with conjugate momenta P_R, P_{θ_1}, and P_{ϕ_1}. In eq C1, we have

$$J'^2\hbar^2 = P_\theta^2 + P_{\theta_1}^2 + 2P_\phi P_{\phi_1} + P_\phi^2 \csc^2\theta + P_{\phi_1}^2 \csc^2\theta_1 + 2P_\theta P_{\theta_1} \cos(\phi - \phi_1) + 2P_\phi P_{\phi_1} \cot\theta \cot\theta_1 \cos(\phi - \phi_1)$$

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$$+ 2P_{\theta_1}P_{\phi} \cot\theta \sin(\phi_1 - \phi) + 2P_{\theta}P_{\phi_1} \cot\theta_1 \sin(\phi - \phi_1) \quad \text{(C2)}$$

In terms of the above coordinates, the Hamiltonian for the interaction between the atom and diatom system is given by the well-known eq C3, written here for later reference

$$H = \frac{1}{2\mu_m}\left[p_r{}^2 + \frac{1}{r^2}\left(P_\theta{}^2 + \frac{P_\phi{}^2}{\sin^2\theta}\right)\right] + \frac{1}{2\mu}\left[P_R{}^2 + \frac{1}{R^2}\left(P_{\theta_1}{}^2 + \frac{P_{\phi_1}{}^2}{\sin^2\theta_1}\right)\right] + V \quad \text{(C3)}$$

where V is the potential energy function for the triatomic system, μ_m is the reduced mass of the diatomic molecule, and μ again is the reduced mass of the atom−diatom system.

In eq C1, one can write

$$\delta(E - E'') = \frac{\delta(P_R - P_R')}{\partial H/\partial P_R} = \frac{\delta(P_R - P_R')}{P_R/\mu}$$

Integration over P_R then yields a P_R' defined by the remaining variables in eq C3.[52] The $\delta(J - J')$ in eq C1 can be written as

$$\delta(J - J') = \frac{\delta(P_\phi - P_\phi')}{\partial J'/\partial P_\phi} = \delta(P_\phi - P_\phi') \quad \text{(C4)}$$

The second equality in eq C4 applies when J is placed along the z-axis; we have $J\hbar = P_\phi + P_{\phi_1}$. It is intuitively evident, since when J is placed along the z-axis we have for the variation in J, $\delta J\hbar = \delta P_\phi$ at constant P_{ϕ_1}. To show the second equality more formally, Cartesian components of the angular momenta corresponding to l and j can be introduced:

$$J^2 = (j_x + l_x)^2 + (j_y + l_y)^2 + (j_z + l_z)^2 \quad \text{(C5)}$$

Taking variations, δ's, of both sides at constant j_z (constant P_{ϕ_1}) and then placing J along the z-axis, i.e., then setting $j_x + l_x = j_y + l_y = 0$ and $j_z + l_z = J$, we have $\delta J\hbar = \delta P_\phi$, i.e., $1/(\partial J\hbar/\partial P_\phi) = 1$, thus yielding eq C4. The factor $1/(\partial J'/\partial P_\phi)$ in eq C4 also serves as a conditional probability: the probability that P_ϕ lies in $(P_\phi, P_\phi + \mathrm{d}P_\phi)$ given that J lies in $(J, J + \mathrm{d}J)$ is $1/(\partial J/\partial P_\phi)$.

We next introduce into eq C2 a new variable $u = \phi - \phi_1$, and thus, (u,ϕ_1) are now variables instead of (ϕ,ϕ_1). At a fixed u, the ϕ_1 can be integrated to yield 2π. Integration over P_ϕ yields P_ϕ', defined by the remaining variables in eq C2 for the given J. The remaining integration in eq C1 is over $\mathrm{d}P_\theta \mathrm{d}P_{\theta_1} \mathrm{d}P_{\phi_1} \mathrm{d}p_r \mathrm{d}\theta \mathrm{d}\theta_1 \mathrm{d}u \mathrm{d}r \mathrm{d}R$. The density of states of the intermediate complex at a given total energy E and J is independent of the orientation of J. If reducing the dimensionality of the integral by one, the vector corresponding to J is placed along the z-axis, yielding the constraint $P_\phi + P_{\phi_1} = J\hbar$.

The limits of integration for the remaining variables in eq C1 are $(0,\pi)$ for θ,θ_1, $(0,2\pi)$ for u, and the limits for r, R and the remaining momenta, subject to the constraints described above, are selected so as to cover the physical range occupied by the intermediate. These variables are randomly sampled in accordance with the microcanonical distribution.

In the various equations given earlier for the interaction region, positive and negative momenta arise. One can use the symmetry to reduce the size of the integration region and avoid potential sign problems. There are eight combinations of signs for $P_{\theta_1}, P_\phi, P_{\phi_1}$: (+,+,+), (+,−,+), (−,+,+), (+,+,−), and the inverse sign for each. The second four combinations can be omitted and the final result multiplied by a factor of 2. For integrating p_r, it suffices to use $p_r \geq 0$ and multiply the final result by 2. The relation[24] $\cos\gamma = \cos\theta\cos\theta_1 + \sin\theta\sin\theta_1\cos u$ can be used to see if γ, the angle between **r** and **R**, corresponds to the molecule ABC or ACB.

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