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A comparison of classical trajectory and statistical unimolecular rate theory calculations of Al\textsubscript{3} decomposition

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Classical trajectories are used to simulate the dissociation of microcanonical ensembles of Al\textsubscript{3} clusters with 0.25-2.00 kcal/mol energy in excess of the dissociation threshold. Unimolecular lifetime distributions for the ensembles are in accord with the random lifetime prescription of Rice–Ramsperger–Kassel–Marcus (RRKM) theory and Al\textsubscript{3} is identified as an intrinsic RRKM molecule. Unimolecular rate constants determined from the trajectories are compared with the predictions of variational RRKM theory with harmonic vibrator and flexible transition state models, phase space theory (PST), and the orbiting transition state model of phase space theory (OTS/PST). The flexible RRKM model, PST, and OTS/PST give Al\textsubscript{2}--Al transition state sums of state which agree to within 1\%. The harmonic vibrator RRKM model gives a sum of states which varies from only 40\% to 10\% larger as the excess energy is increased from 0.25 to 2.0 kcal/mol. Adiabatic switching and direct integration of the phase integral are used to determine the reactant Al\textsubscript{3} anharmonic density of states. For the energies considered in this work, anharmonicity determined by adiabatic switching increases the Al\textsubscript{3} density of states from the harmonic value by a factor of 2.5–2.9. The anharmonic density of states determined by solving the phase integral depends on where the reactant/product phase space boundary is positioned. Placing it at the vibrator transition state gives an anharmonic density of states nearly the same as that determined by adiabatic switching, while placing it at the looser flexible transition state gives a density of states 35\% larger at the highest energy. Using this latter anharmonic density of states gives OTS/PST and flexible RRKM unimolecular rate constants which agree with the trajectory results to within 25\% at the lowest energy and 10\% at the highest energy. Product energy partitioning distributions determined from the trajectories are compared with the predictions of PST, OTS/PST, and the Engelking model. Both OTS/PST and PST give product energy partitioning distributions which are in near quantitative agreement with the trajectory results.

I. INTRODUCTION

The physics and chemistry of clusters is of considerable interest.\textsuperscript{1-6} Clusters allow one to study the transitions from molecular to solid-state properties,\textsuperscript{7} to model surface processes, and to study the effect of solvation on chemical reactivity.\textsuperscript{8,9} Properties of metal and semiconductor clusters have attracted a particularly large amount of attention.\textsuperscript{10-16} Small charged clusters have been widely investigated, partly due to their importance in interpreting mass spectra obtained during nozzle beam expansion experiments.\textsuperscript{17} Unimolecular rate constants, branching ratios, and thresholds have been studied for these clusters. Both theoretical and experimental approaches have been applied to understand the dynamics of rare gas and alkali clusters,\textsuperscript{18-28} and statistical models have been used to analyze cluster decomposition, unimolecular decay rates,\textsuperscript{20-26} binding energies,\textsuperscript{24,26,27} product size distributions,\textsuperscript{25} and product energy partitioning.\textsuperscript{18,22,23,28} Theoretical chemical dynamics studies are particularly relevant, since they provide a link between potential energy surfaces determined by electronic structure calculations and experimental measurements of the chemical dynamics. However, due to the shortage of available potential energy surfaces, only a small number of theoretical studies have been reported of semiconductor and transition metal cluster chemical dynamics.\textsuperscript{29-32}

There is considerable information available concerning aluminum clusters and chemical dynamics calculations for them would be very useful. Extensive electronic structure calculations have been reported for aluminum clusters,\textsuperscript{12,33-48} from which an analytic potential energy surface has been derived.\textsuperscript{34} Other analytic potential energy surfaces have been derived for aluminum clusters by either fitting the phonon dispersion curves and elasticity constants of aluminum,\textsuperscript{49} or dimer data and the bulk cohesive energy to reproduce structures and energetics of aluminum face-centered cubic (fcc) microclusters.\textsuperscript{50} There are a large number of spectroscopic studies of aluminum clusters, many of which provide evidence that the electronic shell model\textsuperscript{16,51} of free electron metals successfully describes electronic properties, ionization potentials, and relative energies.\textsuperscript{15,52-58} Other experiments involving neutral and ionic aluminum clusters have dealt with their oxidation\textsuperscript{59-68} and reactivity towards a variety of reagents,\textsuperscript{59-71} chemisorption on their surfaces,\textsuperscript{67-70} and their collision\textsuperscript{59,60,71-74} and photoinduced\textsuperscript{74,75} unimolecular decomposition. Statistical unimolecular rate theories have been used to interpret these latter experiments. In particular, a simplified Rice–Ramsperger–Kassel–Marcus (RRKM)\textsuperscript{76-78} model has been used to analyze the photodissociation of aluminum cluster cations.\textsuperscript{75}

In the work presented here classical trajectory and detailed statistical unimolecular rate theory calculations are used to study the decomposition of vibrationally excited Al\textsubscript{3}
clusters. The goals of this research are to: (1) determine whether the unimolecular decomposition of Al₃ is intrinsically RRKM; (2) calculate the “exact” anharmonic classical microcanonical rate constant for Al₃ decomposition and compare it with the predictions of various unimolecular rate theories; (3) evaluate the effect of anharmonicity on the Al₃ microcanonical rate constant and develop an anharmonicity correction function; and (4) compare the trajectory Al₂+Al product energy partitioning with the predictions of statistical models. The theories used here to calculate the microcanonical unimolecular rate constant are variational RRKM theory,76-79 with both vibrato,80 and flexible transition states,81 phase space theory,82-85 and the orbiting transition state model of phase space theory.86 The latter model, phase space theory, and the Engeliqing model are used to calculate product energy distributions.

Critical components in statistical rate theories are the molecular sums and densities of states, whose harmonic form is usually used.87,88 An important part of the work presented here is to establish the importance of including anharmonicity when using statistical theories to calculate the Al₃ microcanonical unimolecular decomposition rate constant. The classical anharmonic RRKM unimolecular rate constant can be determined by using either trajectories89-91 or Monte Carlo sampling methods92-98 to simulate the initial decomposition of a microcanonical ensemble. Anharmonicity in both the transition state and the energized reactant are included in these classical trajectory and Monte Carlo calculations of the RRKM rate constant. Thus, a comparison of the classical anharmonic and classical harmonic RRKM rate constants gives a complete anharmonic correction to the harmonic rate constant.89,99-101

Anharmonicity can also be treated by inserting anharmonic densities of states in statistical theory calculations, or by using anharmonicity correction factors for the molecular densities of states.102-104 Such correction functions have been found analytically for stretch anharmonicity by representing the molecule as a collection of uncoupled Morse oscillators105 or a collection of uncoupled mixed harmonic/Morse oscillators.106 As a departure from the traditional (harmonic) normal mode RRKM theory, a Morse RRKM model has also been proposed, in which transition state sum of states and reactant density of states are evaluated explicitly with all molecular bonds being represented by Morse potential functions.107 However, the aforementioned approaches are approximate and neglect other anharmonicity terms, such as bend–stretch coupling, which may be as important as Morse stretch anharmonicity.108,109 Anharmonicity has also been partially introduced in statistical rate theory calculations by evaluating the energy levels of some anharmonic vibrations with semiclassical Wentzel–Kramers–Brillouin (WKB) quantization,109,110 perturbation theory treatment for a given force field,111,112 or by just using Morse energy levels for some anharmonic vibrations.110

Exact classical anharmonic densities of states can be found by evaluating the energy derivative of the molecular phase space volume,87,88 either analytically,104 or by a Monte Carlo approach.89,113-116 Recently, a novel approach based on adiabatic switching was proposed by Reinhardt,117,118 and successfully applied to evaluate exact classical densities of states for water molecules119 and argon clusters.120 In the work presented here, both the classical anharmonic RRKM rate constant and the classical anharmonic molecular density of states are determined for Al₃. It is hoped that this work will provide insight into importance of anharmonicity for clusters and fluxional molecules.

II. POTENTIAL ENERGY SURFACE

The potential energy surface used here was derived from ab initio calculations for Alₙ clusters.34 It consists of two-body Lennard-Jones potential functions V_ij and three-body Axilrod–Teller potential functions120 V_ijk = e^\frac{1}{(r_{ij}r_{jk})^{1/2}} - (r_{ij}r_{jk}r_{ki})^{1/3}, (1)

V_{ijk} = Z \epsilon r_0^6 \left( \cos \alpha_i \cos \alpha_j \cos \alpha_k \right) \frac{1}{(r_{ij}r_{jk}r_{ki})^{1/3}}. (2)

In these equations r_0 is the dimer equilibrium bond length, \epsilon is the bond energy, r_{ij}, r_{jk}, r_{ki}, \alpha_i, \alpha_j, \alpha_k represent the sides and angles, respectively, of the triangle formed by the three atoms i, j, and k, and Z is just an adjustable parameter. Values of 26.52 kcal/mol and 2.635 Å were chosen34 for \epsilon and r_0, respectively, to reproduce the average of ab initio results34 for the nearly degenerate two low-lying 3Π_u and 3Σ_g states of Al₂ (the ground state is 3Π_u,121-123.551,122 and lies no more than 200 cm⁻¹ below the 3Σ_g⁻ state35,121,122). A value of 0.5 was chosen for Z to yield small cluster minimum energy structures in reasonable agreement with the ab initio calculations.34

High-level ab initio calculations by Upton and Bauschlicher et al.35 give 29.3 and 32.0 kcal/mol, respectively, for the Al₂ (3Π_u) bond dissociation, while a recent experiment gives 30.9±1.4 kcal/mol.123 These values are slightly higher than that for the analytic potential used here. The analytic potential gives a harmonic frequency of 490 cm⁻¹ for Al₂. In contrast, the ab initio value by Upton for the 3Π_u and 3Σ_g⁻ harmonic frequencies are 281 and 354 cm⁻¹, respectively.35

Bauschlicher et al. found 278 and 345 cm⁻¹ for these frequencies from their ab initio calculations.35 The experimental harmonic frequency for the 3Π_u state is 285 cm⁻¹,123,124 while for the 3Σ_g⁻ state the frequency is 350 cm⁻¹.123,125 The difference between the Al₂ harmonic frequency from the analytic potential and the ab initio or experimental frequencies for the 3Π_u and 3Σ_g⁻ states is not surprising, since no attempt was made to fit these frequencies in deriving the analytic potential.

The analytic potential energy function of Eqs. (1) and (2) gives two potential energy minima for Al₃. The deepest energy minimum is an equilateral triangle and the other has a linear geometry. Properties of these two minima are listed in Table 1. The potential energies and bond lengths for the two minima reproduce ab initio results34 for the nearly degenerate 4A₂ and 2B₁ states and the slightly higher energy 4B₁ state, all with triangular geometries, and the higher energy 4Σ_u⁻ state with a linear geometry. The analytic potential energy surface has a ~9.0 kcal/mol barrier for going from the triangular to linear geometry.
TABLE I. Properties of the aluminum trimer minimum energy geometries.\(^a\)

<table>
<thead>
<tr>
<th>Property</th>
<th>(\text{Al}_3) (triangle)(^b)</th>
<th>(\text{Al}_3) (linear)</th>
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<tr>
<td>(r_o) (Å)(^c)</td>
<td>2.712</td>
<td>2.612</td>
</tr>
<tr>
<td>(v) (cm(^{-1}))(^d)</td>
<td>307(2), 514</td>
<td>40(2), 365, 658</td>
</tr>
<tr>
<td>(e_o) (kcallmol)(^f)</td>
<td>36.97</td>
<td>30.82</td>
</tr>
</tbody>
</table>

\(^a\)Properties are for the analytic function of Eqs. (1) and (2).
\(^b\)The triangle is equilateral.
\(^c\)Equilibrium bond lengths.
\(^d\)Vibrational frequencies.
\(^e\)\(\text{Al}_2\rightarrow\text{Al}_3+\text{Al}\) classical dissociation threshold.

The \textit{ab initio} calculations by Bauschlicher et al. give a \(\text{Al}_3\rightarrow\text{Al}_2+\text{Al}\) classical threshold \(e_o\) of 35.7 kcal/mol for both the \(^4\text{A}_2\) and \(^2\text{A}_1\) states.\(^{34}\) They find that the almost equilateral triangle \(^2\text{A}_1\) state has equilibrium bond lengths \(r_0\) of 2.59 Å, while the \(^4\text{A}_2\) state has two bond lengths of 2.62 Å and one of 3.04 Å. In his \textit{ab initio} calculation,\(^{38}\) Upton finds \(e_o\) of 38.4 kcal/mol and a bond length of \(\sim 2.62\) Å for the almost equilateral triangle \(^2\text{A}_1\) state, while he finds two bond lengths of 2.64 and one of 3.04 Å for the \(^4\text{A}_2\) state. From a series of high-level \textit{ab initio} calculations,\(^{43}\) Tse estimates the “best” value bond lengths would be \(r_0=2.57\) Å for the \(^2\text{A}_1\) state and \(r_0=2.63(2)\) and 3.19 Å for the \(^4\text{A}_2\) state. He also determined harmonic vibrational frequencies. They are 289, 164, and 163 cm\(^{-1}\) for the \(^2\text{A}_1\) state and 247, 233, and 96 cm\(^{-1}\) for the \(^4\text{A}_2\) state. For the linear \(^2\Sigma^+\) state, Bauschlicher et al. calculate an \(\text{Al}−\text{Al}\) equilibrium bond length of 2.62 Å and an \(e_o\) of 26.3 kcal/mol.\(^{34}\) There have been no definitive experimental determinations of structural and/or threshold energies for any of the \(\text{Al}_3\) electronic states. However, an upper limit of 55 kcal/mol has been placed on the \(\text{Al}_2−\text{Al}\) dissociation energy.\(^{126}\)

As discussed above, in deriving the analytic potential energy function for \(\text{Al}_3\rightarrow\text{Al}_2+\text{Al}\), Eqs. (1) and (2),\(^{34}\) geometries, and energies are used, which are averages of those for the low-lying nearly degenerate electronic states of \(\text{Al}_2\) and \(\text{Al}_3\). This seems to be a reasonable approach, since there should be extensive state mixing for a fluxional molecule like \(\text{Al}_3\). The potential energy functions of Eqs. (1) and (2) are standard options in the general chemical dynamics computer program \textsc{Venus}.\(^{127}\) \textsc{Venus} was used to determine the \(\text{Al}_3\rightarrow\text{Al}_2+\text{Al}\) analytic function’s potential minima and their geometries, vibrational frequencies, and dissociation thresholds, which are listed in Table I.

III. CLASSICAL TRAJECTORY METHOD

The classical trajectory simulations\(^{128,129}\) were performed with the general chemical dynamics computer program \textsc{Venus}.\(^{127}\) Initial coordinates \(q\) and momenta \(p\) were chosen for \(\text{Al}_3\) to simulate a reactant microcanonical ensemble (i.e., total energy \(E\) is constant and the reactant phase space is sampled randomly) at total angular momentum \(J\) of zero. Both microcanonical normal mode sampling\(^{130}\) and orthant sampling,\(^{11,131}\) which are standard options in \textsc{Venus}, were used to choose initial conditions. These sampling schemes do not give an exact microcanonical ensemble\(^{59}\) and, thus, may give a sampling transient at short times if intrinsic chaotic motion of the trajectories does not quickly form an exact reactant microcanonical ensemble. As will be shown in Sec. V this latter condition is met for \(\text{Al}_3\). For example, initially exciting the normal modes of the triangular \(\text{Al}_3\) minimum gives nearly the same decomposition rate constant as does exciting the normal modes of the linear \(\text{Al}_3\) minimum.

Orthant sampling requires a scaling factor, denoted \(P_{\text{scale}}\), so that the average kinetic/potential energy ratio \((\langle T\rangle)/(\langle V\rangle)\) for the initial conditions is the same as that for individual trajectories integrated for long times.\(^{132}\) The ratio \((\langle T\rangle)/(\langle V\rangle)\) for the initial conditions selected here is in the range 1.0–1.1, which requires \(P_{\text{scale}}^{-2.0}\). Orthant sampling also requires a limiting value for the \(\text{Al}_2+\text{Al}\) center-of-mass separation, to define maximum coordinate displacements for sampling the reactant phase space. The vibrator transition state structure (see Sec. III C) was used to identify the limiting center-of-mass separation. Limits are not placed on the coordinates in microcanonical normal mode sampling.

The trajectories are evaluated by solving Hamilton’s equations of motion\(^{133}\)

\[
\frac{dq}{dt} = \frac{\partial H}{\partial p}, \quad \frac{dp}{dt} = -\frac{\partial H}{\partial q},
\]

where \(H\) is the Hamiltonian. The expressions in Eq. (3) form a set of coupled differential equations which are integrated by a combined fourth-order Runge–Kutta and a sixth-order Adams–Moulton predictor–corrector algorithm.\(^{125}\) The integrations are performed with a stepsize of 0.1 fs, which ensures energy conservation to at least seven places along a trajectory. The ensembles contain 200 trajectories and the vibrational energy range investigated here is 0.0–2.0 kcal/mol above the reaction threshold. With vibrational energies greater than 2.0 kcal/mol above the threshold, clusters dissociate even before a period of the smallest vibration has been completed, not allowing intermolecular vibrational energy redistribution (IVR) between the molecular modes to occur before dissociation. Thus, sampling transients may occur at these energies.

The dissociation time (or lifetime) of a vibrationally excited \(\text{Al}_3\) cluster is defined dynamically\(^{134}\) as the particular time the kinetic energy of the evaporating atom stops oscillating and becomes a monotonically decreasing function of time, asymptotically approaching zero. As illustrated in Fig. 1, the atomic kinetic energy keeps oscillating because of the continuous internal vibrational energy exchange between the molecular modes, as long as the atom is bound to the others. This approach has been successfully used for Lennard-Jones clusters\(^{134}\) and, although it might not work for nonmonomer evaporation, it is satisfactory for our study of \(\text{Al}_3\) clusters.

When the trajectory is finished a final product analysis is performed and various classical mechanical molecular properties, such as relative translational energy, orbital and rotational angular momenta, centrifugal energy, and product vibrational and rotational energies, are calculated from the atomic Cartesian coordinates and momenta.\(^{128,129}\) The \(\text{Al}_2\) internal energy is separated into vibrational and rotational energies by calculating an average \(\text{Al}_2\) vibrational energy for a few (about seven or eight) \(\text{Al}_2\) vibrational periods. Both
unimolecular rate constants and product energy distributions are calculated and details of the computational procedure are given in Sec. V along with the results. All uncertainties presented here are given for a 99% confidence level, unless specified otherwise.

IV. STATISTICAL UNIMOLECULAR RATE THEORY CALCULATIONS

In this section statistical rate theory calculations are presented for the microcanonical decomposition rate and product energy distributions of vibrationally excited Al₃ clusters. According to the microcanonical transition state theory of unimolecular reactions, i.e., RRKM theory, the unimolecular rate constant, as a function of energy \( E \) and total angular momentum \( J \), is given by

\[
k(E, J) = \frac{L_0^3 \ N_0^2(E, J)}{\hbar^2 \ \rho(E, J)^3},
\]

(4)

where \( h \) is Planck’s constant, \( N_0^2(E, J) \) is the sum of states for the active degrees of freedom in the transition state, \( L_0^3 \) is the reaction channel statistical factor, and \( \rho(E, J) \) is the density of states for the active degrees of freedom in the reactant at total energy \( E \). In the following, the angular momentum dependence of the above physical quantities will be omitted since the present study only deals with nonrotating \( J = 0 \) clusters. A critical component in statistical rate theories is the density of states \( \rho(E) \) for the reactant molecule. For a fluxional molecule like Al₃, which has two potential minima with triangular and linear structures, special consideration must be given in determining \( \rho(E) \) and the microcanonical unimolecular rate constant.

A. Microcanonical rate constant and effective density of states for a fluxional molecule

The problem for Al₃ is to find the unimolecular rate constant for the dissociation of a microcanonical ensemble of two isomers. The isomerization of the two isomers is defined by

\[
\frac{k_1}{k_2} \quad \text{Al}_1 \rightarrow \text{Al}_2.
\]

(5)

For the first case considered here, it will be assumed that only isomer Al₁ dissociates; i.e.,

\[
k_d \quad \text{Al}_1 \rightarrow \text{Products}.
\]

(6)

The microcanonical rate for Al₃ dissociation is then

\[
R = k_{\text{mic}}(n_1 + n_2) = k_d n_1,
\]

(7)

where \( k_{\text{mic}} \) is the microcanonical rate constant, \( n_i \) is the number of \( \text{Al}_i \) molecules in the ensemble \( (i = 1, 2) \). Combining the equilibrium condition for a microcanonical ensemble, \( k_d n_1 = k_d n_2 \), with Eq. (7) yields the following expression for the microcanonical rate constant:

\[
k_{\text{mic}} = k_d \frac{k_2}{k_1 + k_2}.
\]

(8)

Since the transition state for the forward and reverse reactions of the chemical equilibrium in Eq. (5) is the same, the ratio of the RRKM rate constants \( k_1 \) and \( k_2 \) given by Eq. (4), only depends on the densities of states of both isomer reactants and the reaction channel statistical factors. The statistical factor is the symmetry number ratio of reactant to transition state; i.e., \( L^3 = \sigma_2^3 \sigma_1^3 \). Thus, the ratio of the RRKM rate constants \( k_1 \) and \( k_2 \) becomes

\[
\frac{k_2(E)}{k_1(E)} = \frac{\sigma_2^3}{\rho_2(E) \left( \frac{\sigma_1^3}{\rho_1(E)} \right)^{-1}},
\]

(9)

where \( \sigma_i \) denotes the symmetry number of isomer \( \text{Al}_i \). Equation (9) maintains the basic property of a microcanonical ensemble in equilibrium; i.e., the number of molecules of a given molecular species is proportional to its effective density of states. Since \( \rho_i(E) \) is the density of states over the phase space, for isomer \( \text{Al}_i \) and \( \sigma_i \) is just the factor introduced to avoid overcounting indistinguishable configurations in phase space, the number of molecules of isomer \( i \) obeys

\[
n_i(E) \approx \frac{\rho_i(E)}{\sigma_i}.
\]

(10)

By combining Eqs. (8) and (9), the microcanonical rate constant becomes

\[
k_{\text{mic}}(E) = k_d(E) \frac{\rho_1(E) / \sigma_1}{\rho_1(E) / \sigma_1 + \rho_2(E) / \sigma_2}.
\]

(11)

Since the RRKM rate constant \( k_d \) in Eq. (6) is

\[
k_d(E) = \frac{N_0^2(E) / \sigma_0^3}{h \rho_1(E) / \sigma_1},
\]

(12)

where \( N_0^2(E) \) and \( \sigma_0^3 \) are the transition state sum of states and symmetry number, respectively, the microcanonical rate constant can be written as

\[
k_{\text{mic}}(E) = \frac{1}{h} \frac{N_0^2(E) / \sigma_0^3}{\rho_1(E) / \sigma_1 + \rho_2(E) / \sigma_2}.
\]

(13)

Comparing Eqs. (4) and (13) shows that the effective reactant density of states is...
For the Al₃ trajectories calculated here the total angular momentum is zero, so that the molecular motion is confined to a plane. Thus, in the calculations reported below, which use this reaction path information, only one of the degenerate bending degrees of freedom for the linear reaction path is included.

### C. Variational RRKM theory

For a unimolecular reaction which has a barrierless reverse association reaction, variational RRKM theory has yielded good results in a number of applications. In this theory, properties of the molecular system such as potential energy, moments of inertia, and vibrational frequencies are required along the reaction path in order to find the minimum in the sum of states which identifies the transition state. In this work, both vibrator and flexible models are considered for the variational transition state.

#### 1. Harmonic vibrator transition state model

For a nonrotating (J=0) molecular system, the harmonic vibrational sum of states for a point along the reaction path r is given by

\[
N(E) = \left( \frac{E - V(r)}{\Delta E} \right)^{s-1} \prod_{j=1}^{s-1} \frac{1}{\pi} v_j(r),
\]

where \(V(r)\) and \(v_j(r)\) are the classical potential energy and vibrational frequencies, respectively, as a function of the reaction path, and \(s\) is the number of degrees of freedom of the molecular system. For \(\text{Al}_3\rightarrow\text{Al}_2+\text{Al}\) dissociation confined to a plane \(s=3\). The two \(v_j\) vibrational frequencies are the \(\text{Al}-\text{Al}\) bending and the \(\text{Al}-\text{Al}\) stretch. \(N(E)\) in Eq. (19) is minimized vs \(r\) to find the harmonic vibrator variational transition state.

The results of these calculations are listed in Table II. As shown from previous work, the transition state "tightens" as the energy in excess of the classical threshold \(E_{\infty}\) is increased from 0.25 to 2.0 kcal/mol; i.e., \(r^+\) shortens and the \(\text{Al}-\text{Al}-\text{Al}\) stretch frequency at the transition state increases from 4.4 to 15.6 cm⁻¹. It is also of interest that the \(\text{Al}-\text{Al}\) stretching frequency changes by less than 0.5% in going from the dimer product to the variational transition state. Thus, it is quite accurate to treat this stretch as a "conserved" mode.

#### 2. Flexible transition state model

A possible shortcoming of the above vibrator transition state model is that it treats the low-frequency \(\text{Al}-\text{Al}-\text{Al}\) bend as a harmonic oscillator. It might be more appropriate to treat this mode, called a "transitional" mode, as a hindered rotor and this is done in the flexible transition state model. For this model the transition state sum of states can be written as a convolution

\[
N(E) = \int_0^{E-V(r)} \rho_0 E - V(r) - \epsilon_{\text{TR}} N_{\text{TR}}(\epsilon_{\text{TR}}) d\epsilon_{\text{TR}},
\]

where \(\rho_0\) is the density of states for the conserved modes, \(N_{\text{TR}}\) is the sum of states for the transitional modes, and \(\epsilon_{\text{TR}}\) is the transitional mode energy. \(N_{\text{TR}}\) is determined by representing the transitional modes by the long-range product Hamiltonian
TABLE II. Properties of different models for the Al₃→Al₂⁺Al transition states.

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<thead>
<tr>
<th></th>
<th>r(^2)</th>
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</tbody>
</table>

\(^a\)Energies are in kcal/mol, reaction coordinate in Å, and angular momenta in h.
\(^b\)Energy in excess of the product asymptotic limit.
\(^c\)Al₂⁺Al center-of-mass separation at the transition state.
\(^d\)Internal energy of the transition state.
\(^e\)Maximum possible orbital angular momentum.
\(^f\)Transition state sum of states.
\(^g\)Not relevant to the variational transition state.
\(^h\)Anharmonicity is included in both the conserved and transitional modes; see the text.
\(^i\)Anharmonicity is included in the product Al₂ vibration, which increases the sum of states by less than 2%.
\(^j\)Minimum Al₂⁺Al center-of-mass separation allowed at the centrifugal barrier for the orbiting transition state.

The classical sum of states \(N(E)\) is the phase space volume enclosed by the energy shell, divided by Planck’s constant for each degree of freedom.\(^87,138\) For the Al₂⁺Al transition state Hamiltonian in Eq. (21) becomes

\[
H(r, \theta) = \frac{I^2}{2I(r)} + V_{TR}(r, \theta),
\]

(22)

The reduced moment of inertia is given by

\[
I(r) = \left( \frac{1}{\mu_0 R^2} + \frac{1}{2 \mu r^2} \right)^{-1},
\]

(23)

where \(R\) and \(\mu_0\) are the diatomic bond length and reduced mass, respectively, \(V_{TR}(r, \theta)\) is the transitional mode potential, and \(\theta\) is the angle between \(R\) and \(r\). The rotational or orbital angular momentum action \((j \text{ or } l \text{ expressed in } \hbar \text{ units})\) and \(\theta\) are conjugate action-angle variables.\(^133,138\) \(V_{TR}(r, \theta)\) was evaluated during the course of the reaction path following calculations for Al₂⁺Al→Al₁ and was found to be accurately represented by the following simple analytic function first proposed by Pacey:\(^159\)

\[
V_{TR}(r, \theta) = V_0(r) \sin^2 \theta.
\]

(24)

The \(V_{TR}(r, \theta)\) given by the analytic potential energy function, Eqs. (1) and (2), and by the fit of Eq. (24) are compared in Fig. 2.

The classical sum of states \(N(E)\) is the phase space volume enclosed by the energy shell, divided by Planck’s constant for each degree of freedom.\(^87,138\) For the Al₂⁺Al transition state Hamiltonian in Eq. (22) there is only one degree of freedom with momentum \(j\) and conjugate coordi-
This integral is an elliptic integral and its integration was phase space theory by Light and co-workers82,161 and amend­
energy.82-86,161-164 Explicit in the initial development’ of
are listed in Table III. They are less than 5% greater than the
grate over
assumes the decomposition of a molecule or a collision com­
tion state limit assumes that the reaction potential energy
ction state is increased.

\[ N_{T} = \frac{1}{\hbar} \sin^{-1} \left( \frac{\sqrt{E - E_0}}{V_0} \right) \sin^2 \theta \ d\theta \]  

with \( \theta_{\max} = \sin^{-1} \sqrt{E/E_0} \) if \( E \leq V_0 \) and \( \theta_{\max} = \pi/2 \) otherwise. This integral is an elliptic integral and its integration was carried out numerically by Gaussian quadrature.160 The transition state sum of states in Eq. (20) is then determined numerically by Gaussian quadrature.

The anharmonic Al2 vibrational density of states was determined by evaluating the phase space volume associated with the Al2 vibrational Hamiltonian and then differentiating this volume with respect to energy. The resulting densities are listed in Table III. They are less than 5% greater than the harmonic density which is energy independent and equals 1/\( h \nu \), which yields the constant value 2.04 \times 10^{-3} \text{cm}^{-1}.

Properties of the flexible variational transition states are listed in Table II, where they are compared with those of the harmonic vibrator variational transition states. It is seen that \( \mathcal{R} \) is larger and \( \mathcal{N} \) is 10%-30% smaller for the flexible variational transition states. The difference between \( \mathcal{N} \) for the vibrator and flexible transition states decreases as energy is increased.

D. Phase space theory and orbiting transition state/ phase space theory

1. Rate constant

Phase space theory (PST) is a statistical theory which assumes the decomposition of a molecule or a collision complex is governed by the phase space available to each product under strict conservation of angular momentum and energy.82-86,161-164 Explicit in the initial development of phase space theory by Light and co-workers82,161 and amendments by Klots83-85 is a loose transition state with properties identical to those of the reaction products. This loose transition state limit assumes that the reaction potential energy surface is of no importance in determining the unimolecular rate constant. The PST differential unimolecular rate constant for forming products with total angular momentum \( J \) and energy \( E_u \) is given by,

\[ R(E,J,E_u) = \frac{L^* \rho^*(E) \Gamma^*(E_u,J)}{h \rho(E)} \]  

where \( L^* \) is the reaction channel statistical factor, \( \rho^*(E) \) is the vibrational density of states of the products at energy \( E \), \( E_u \) is the energy difference between reactants and products, and \( \Gamma^*(E_u,J) \) is the product sum of rotational-orbital states with rotational-orbital energy less than or equal to \( E \), \( \rho(E,J) \) is the density of states of the reactant at energy \( E \) and total angular momentum \( J \), and \( E_u \) is the sum of product translational and rotational energies:

\[ E_u = E_r + E_r. \]  

The microcanonical unimolecular reaction rate constant is then the convolution

\[ k(E,J) = \int_0^{E-E_0} R(E,J,E_u) dE_u \]  

\[ = \frac{L^* \rho^*(E-E_0) \Gamma^*(E_u,J)}{h \rho(E,J)} \int_0^{E-E_0} \rho^*(E-E_0) \Gamma^*(E_u,J) dE_u. \]  

As shown in Appendix A, for this study, the PST rate constant is expressed as

\[ k(E) = \frac{L^* \rho^*(E) \Gamma^*(E_u,J)}{h \rho(E)} \left( \frac{E_u}{B_r} \right)^{S} dE_u, \]  

where \( S=1/2 \).165 This equation is generally applicable to systems with \( J=0 \), and Klots has tabulated values of \( S \) and \( B \), for various reaction products (i.e., sphere–sphere, sphere–atom, linear–atom, etc.).165 Comparing Eq. (29) with Eq. (4) shows that the PST transition state sum of states is given by the integral in Eq. (29). The integration is performed numerically by Gaussian quadrature.160 The resulting sums of states, with Al2 treated as an anharmonic oscillator, are listed in Table II. They are 10%-30% smaller than the sums of states for the harmonic vibrator variational transition states, and


\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Energy} & \textbf{Harmonic} & \textbf{Anharmonic} & \textbf{Harmonic} & \textbf{Anharmonic} & \textbf{Harmonic} & \textbf{Anharmonic} \\
\hline
\textbf{Linear Al3} & & & & & & \\
0.00 & 6.09 & 13.08±0.52 & 1.73 & 8.21±0.19 & 3.62 & 9.28±0.33 \\
0.25 & 6.19 & 13.75±0.58 & 1.75 & 8.45±0.19 & 3.68 & 9.28±0.33 \\
0.50 & 6.29 & 13.75±0.58 & 1.78 & 8.69±0.20 & 3.74 & 9.77±0.35 \\
0.75 & 6.39 & 13.75±0.58 & 1.80 & 8.85±0.21 & 3.80 & 9.28±0.33 \\
1.00 & 6.50 & 14.55±0.68 & 1.83 & 9.15±0.21 & 3.86 & 10.33±0.36 \\
1.25 & 6.60 & 14.55±0.68 & 1.85 & 9.43±0.22 & 3.92 & 10.33±0.36 \\
1.50 & 6.70 & 15.55±0.62 & 1.87 & 9.49±0.22 & 3.98 & 10.94±0.38 \\
1.75 & 6.81 & 15.55±0.62 & 1.90 & 9.67±0.23 & 4.04 & 12.13±0.36 \\
2.00 & 6.91 & 16.78±0.68 & 1.92 & 9.92±0.24 & 4.10 & 11.70±0.42 \\
\hline
\end{tabular}
E. Anharmonic $\text{Al}_2$ density of states

1. Triangular and linear $\text{Al}_2$ densities by adiabatic switching

Reinhardt\textsuperscript{117,118} has recently proposed a model for calculating anharmonic densities of states, based on the Hertz invariance principle\textsuperscript{167} and Liouville's time-dependent theorem.\textsuperscript{138} Combining these ideas, it was found that, if an ergodic Hamiltonian is changing slowly in time, its energy shell—and therefore its density of states—is an adiabatic invariant, even if the system energy is not.\textsuperscript{118} Thus, when adiabatically switching a Hamiltonian into a reference Hamiltonian, one maps an initial hypersurface at constant energy (i.e., a microcanonical ensemble) into a continuous family of surfaces, each of which is also at constant energy. The idea is to use a reference Hamiltonian for which the classical density of states is known precisely, e.g., separable harmonic Hamiltonian.\textsuperscript{76-78,87,88} Since completely ergodic systems are quite rare, especially those with a few degrees of freedom, Reinhardt proposed to apply the Hertz model by averaging

where $E_a$ is the energy in excess of the classical threshold, $E_p$ is the product (diatom) vibrational energy, $E_{\text{int}}$ is the product (diatom) internal vibrational/rotational energy, $E_t$ is the product relative translational energy, $E_r$ is the product translational and rotational kinetic energy, and $E_r$ is the product rotational energy. The kinetic energy release probability density is just the normalized differential rate constant,\textsuperscript{86,164}

\begin{equation}
P(E_r) &= \int \rho_0^2(E_c - E_t - E_p)(E_r)^{S-1} \, dE_r, \tag{33}
\end{equation}

where $S=1/2$, and the product rotational angular momentum probability density is

\begin{equation}
P(E,J) &= \int \rho_0^3(E_c - E_t - B_jJ^2) \, dE_t. \tag{34}
\end{equation}

Equation (33) can be normalized to yield through Eq. (31), the product internal energy distribution. In PST Eqs. (31)–(34) are applied at the product asymptotic limit, and the boundaries in the integrals are determined for this limit. However, in OTS/PST these equations and their integral boundaries are evaluated at the orbiting transition state, which has the effect of adding the height of the centrifugal barrier to $E_t$ to obtain the product translational energy. The remaining energy terms are unaffected and, thus, are the same in PST and OTS/PST. However, as shown in Appendix A their probability distributions are different since the integral boundaries for PST and OTS/PST are different. In Sec. V product energy distribution calculated with PST and OTS/PST are compared with the results of the classical trajectory simulations.
over trajectories. If the final energies of the trajectories which are switched into the reference Hamiltonian do not exhibit a large dispersion, the anharmonic density of states is just that of the reference system with the average final energy; for a harmonic oscillator (ho) reference Hamiltonian this is expressed as

\[ \rho(E) = \rho_{ho}(\bar{E}_{ho}). \] 

(35)

In previous work, the above method has been applied successfully to water molecules\(^{119}\) and argon clusters.\(^{23}\) In this work it is used to evaluate the individual density of states for the Al\(_3\) triangular and linear isomers. The trajectory results presented in Sec. V indicate the Al\(_3\) system is ergodic. An initial microcanonical ensemble is prepared, as discussed in Sec. III, for each of the Al\(_3\) isomers and, while integrating the equations of motion, the anharmonic Al\(_3\) Hamiltonian is switched into a harmonic Hamiltonian; i.e.,

\[ H(p, q, t) = \frac{p^2}{2m} + a(t)V_{ho}(q) + [1 - a(t)]V_{anh}(q), \] 

(36)

where \( V_{anh} \) is the anharmonic Lennard-Jones+Axilrod-Teller Al\(_3\) potential described in Sec. II and used in the trajectory calculations, \( V_{ho} \) is the harmonic potential energy function, and \( a(t) \) is a switching function of the form\(^{118,119}\)

\[ a(t) = \frac{t}{\tau} \sin(2\pi t/\tau) \frac{2\pi}{2\pi} \] 

(37)

with switching time \( \tau \). This switching function has given converged results in previous work.\(^{23,119}\) The integration stepsize is the same as for trajectory calculations and each ensemble contains 1000 trajectories.

The choice of a reference, harmonic in this study, Hamiltonian is usually not critical. However, for linear Al\(_3\), care was required in choosing the bending force constant, so that the ensemble of structures obtained from adiabatic switching is an approximate microcanonical ensemble of linear Al\(_3\) structures for the reference Hamiltonian. For example, using a large bending force constant result in a final ensemble whose structures are linear, but dissociated! To overcome this problem, the harmonic force constants corresponding to the anharmonic Lennard-Jones+Axilrod-Teller Al\(_3\) potential are used with one slight modification. These harmonic force constants can be calculated explicitly\(^{118}\) from the vibrational frequencies listed in Table I for each of the isomers. The three stretching frequencies of triangular Al\(_3\) are fit by a force constant of 1.116 mdyn/\(\text{Å}^2\). For linear Al\(_3\) the two stretching frequencies are fit by a force constant of 2.252 mdyn/\(\text{Å}^2\) and the bending frequency by a force constant of 0.0285 mdyn/\(\text{Å}/\text{rad}^2\). These force constants are used for the harmonic oscillator Hamiltonian, with the modification of adjusting the bending force constant of linear Al\(_3\) so that the final ensemble structures give the same average configuration as for a microcanonical ensemble of harmonic linear Al\(_3\).

Values for the switching time \( \tau \), needed to obtain the required adiabaticity condition have been discussed previously.\(^{117-119}\) As shown in Fig. 4, converged results are obtained with switching times of 5 ps for triangular Al\(_3\) and 20 ps for linear Al\(_3\). These switching times represent between 30 and 50 cluster vibrational periods and are consistent with those used in previous work for argon clusters.\(^{23}\) It is also remarkable that zero total angular momentum for the two Al\(_3\) isomers is well conserved by adiabatic switching, as found from previous work.\(^{23}\)

Anharmonic densities of states calculated with the above approach are listed in Table III, where they are compared with the harmonic densities. For linear Al\(_3\) the anharmonic densities are 2.2–2.4 times larger than the harmonic values, while the triangular Al\(_3\) anharmonic densities are 4.8–5.2 times larger. Also listed are the harmonic and anharmonic effective densities of states \( \rho_{eff}(E) \) divided by the statistical factor \( L^\dagger \). The \( \rho_{eff}(E)/L^\dagger \) can be calculated from either Eq. (14) or (18), since they give the same result. The variational vibrator or flexible transition state has no symmetry, since it is a linear triatomic with different bond lengths, so \( \sigma^2 \) in Eq. (14) is 1. For orbiting transition state/phase space theory, \( \sigma^2_2 \) in Eq. (18) is the symmetry number 2 for the Al\(_2\) product. The symmetry numbers of triangular and linear Al\(_3\) are 3 and 2, respectively. The effective Al\(_3\) anharmonic densities are 2.5–2.9 times larger than the corresponding harmonic densities.

2. Al\(_3\) density of states by solving the phase integral

The Al\(_3\) anharmonic density of states can also be readily evaluated by solving the phase integral for the Al\(_3\) Hamiltonian, since it is only a three degree of freedom system. If the molecular Hamiltonian can be written as\(^{114}\)
The Hamiltonian for a rotationless triatomic molecule such as Al₃ can be written in the form of Eq. (38) and is

\[ H(p, q) = \frac{1}{2} \sum_{i=1}^{3} G_{ii} p_i^2 + V(q), \]  

where the \( G_{ii} \) are functions of the atomic masses and the coordinates \( q \), the momentum phase space volume can be integrated analytically, since it can be reduced to the volume of an \( s \)-dimensional sphere by a proper canonical transformation. The expression for the sum of states then becomes

\[ N(E) = \frac{(2 \pi)^{s/2}}{h^{s/2} \Gamma(1 + s/2)} \int_{v < E} [E - V(q)]^{s/2} dq, \]  

where \( \Gamma \) represents the gamma function.

The Hamiltonian for a rotationless triatomic molecule such as Al₃ can be written in the form of Eq. (38) and is

\[ H = \frac{p_R^2}{2 \mu_0} + \frac{p_r^2}{2 \mu} + \frac{p_\theta^2}{2 I} + V(r, R, \theta), \]  

where \( R \) is the bond length of one of the diatoms, \( r \) is the distance of the third atom from the diatom center-of-mass, \( \theta \) is the angle between \( R \) and \( r \), and \( p_R, p_r, \) and \( p_\theta \) are the conjugate momenta. The effective mass terms \( G_{ii} \) are \( \mu_0 \) and \( \mu \), the reduced masses of the diatom and the atom–diatom, respectively, and \( I \), the reduced moment of inertia as defined in Eq. (23). By making the proper substitutions into Eq. (39) the anharmonic sum of states for Al₃ becomes

\[ N(E) = \frac{4 \pi (2m)^{s/2}}{3\sqrt{3}h^3} \int_{v < E} [E - V(r, R, \theta)]^{3/2} dr dR d\theta, \]  

where \( m \) is the aluminum atomic mass, which is solved numerically by triple Gaussian quadrature. The anharmonic density of states is then simply the derivative of \( N(E) \) with respect to \( E \).

The only difficulty in solving Eq. (41) is for energies greater than the reaction threshold, since the integral becomes unbounded and diverges. In previous work, the boundaries of the phase space integral have been determined by the transition state structure found from harmonic RRKM calculations and this approach is used here. Densities of state given by the vibrator and flexible transition state phase space boundaries are plotted in Fig. 5, where they are compared with the effective anharmonic density of states determined by adiabatic switching. Below the threshold the density determined by adiabatic switching is within 5% of those obtained by directly integrating the phase integral. Above the threshold the difference between the two methods depends upon which transition state structure is used to define the boundaries of the phase space integral. If the vibrator transition state structure is used to define the phase space boundaries, the density from solving the phase integral is only 1%–5% larger than that from adiabatic switching for \( E_r \) in the range 0.0–2.0 kcal/mol. However, using the flexible transition state to identify the phase space boundaries gives densities of state by solving the phase integral which are 1%–35% larger than those by adiabatic switching for the \( E_r \) = 0.0–2.0 kcal/mol energy range. These differences are not extraordinary and, thus, not too disconcerting. But they do point out there is some ambiguity in defining phase space boundaries for a molecular Hamiltonian excited above the unimolecular threshold. It is worth noting that, though solving the phase integral by Monte Carlo or quadrature techniques has been widely used to evaluate classical sums and densities of state, Reinhardt has shown that it is often difficult to converge such procedures when applied to molecular systems with more than four atoms.

F. Anharmonic unimolecular rate constants

The anharmonic densities of state for Al₃, calculated above by adiabatic switching, were fit by a polynomial function of energy and used in statistical rate theory calculations of the Al₃ unimolecular rate constant. As discussed above, anharmonicity is included in the transition state for the flexible variational RRKM and OTS/PST calculations. However, since the transition state energy is quite small, anharmonicity has a negligible effect on the transition state sums of states. For OTS/PST it increases the expected sum of states by less than 2%. Anharmonicity is also expected to have a small effect on the transition state sum of states for the vibrator RRKM model. Thus, the principal effect of anharmonicity is to increase the Al₃ density of states and decrease the unimolecular rate constant.

Anharmonic rate constants calculated in the above manner for the variational RRKM vibrator and flexible models and OTS/PST are listed in Table IV. Harmonic rate constants for the vibrator model can be obtained by multiplying the anharmonic rate constant for this model by the anharmonic/harmonic density of state ratio from Table III. Harmonic rate constants are found in a similar manner for OTS/PST, except an additional multiplicative factor of \( \sim 0.98 \) to 1.00 is used to remove anharmonicity of the Al–Al stretch in the transition state (see Table III). It is difficult to obtain a pure harmonic rate constant for the flexible RRKM model, since anharmon-
TABLE IV. \(A_l_3\rightarrow A_l_2+A_l\) classical anharmonic microcanonical unimolecular rate constants given by variational RRKM and OTS/PST theories.

<table>
<thead>
<tr>
<th>(E_{\text{m}})</th>
<th>RRKM vibrator (TS^b)</th>
<th>RRKM flexible (TS^b)</th>
<th>OTS/PST^c</th>
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<td>171.26 ± 6.14</td>
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<td>153.53 ± 4.51</td>
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Reactant densities of states by solving the phase integral

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<th>(n(0))</th>
<th>(n(0))</th>
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<td>104.97</td>
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</table>

Energies are in kcal/mol and rate constants in ns\(^{-1}\).

Rate constants calculated with a transition state (TS) harmonic sum of states.

Rate constants calculated with a transition state (TS) anharmonic sum of states.

Anharmonic rate constants were also determined by using the \(A_l_3\) densities of state found by directly solving the phase integral, with the phase space boundary for the integral given by the appropriate transition state structure. Anharmonic vibrator and flexible RRKM and OTS/PST rate constants calculated in this manner are listed in Table IV. The \(A_l_3\) anharmonic densities of states calculated with the phase space boundary given by the flexible transition state structure are used in calculating the anharmonic OTS/PST rate constants.

V. TRAJECTORY RESULTS AND COMPARISON WITH STATISTICAL THEORIES

A. Unimolecular rate constants

The unimolecular lifetime distribution is given by\(^{90,91,169}\)

\[
P(\tau) = -\frac{1}{n(0)} \frac{dn}{d\tau},
\]

where \(n(0)\) is the total number of molecules in the ensemble and \(n\) is the number of molecules which have not yet dissociated at time \(\tau\). An essential question to address is whether the lifetime distributions obtained from the classical trajectory calculations agree with RRKM theory,\(^{76-78}\) which predicts a random lifetime distribution\(^{88,90}\)

\[
P(\tau) = k \exp(-k\tau),
\]

where \(k\) is the microcanonical unimolecular rate constant. Everyone of the lifetime distributions calculated here is of the form defined by Eq. (43). An example is illustrated in Fig. 6. For every set of initial conditions sampled in the trajectory calculations, it was found that there was the same number (within statistical uncertainties) of dissociations of each \(A_l\) atom, which is consistent with intrinsic RRKM behavior. However, the ultimate proof of this behavior is the finding, as shown in Fig. 6, that the \(t=0\) intercept of \(P(t)\) is equal to the rate constant in the exponential. The central assumption of RRKM theory, which states that all the accessible molecular states are occupied with equal probability, is then valid, implying that the classical motion is chaotic and the Hamiltonian system is presumably ergodic.\(^{78}\)

RRKM theory predicts exponential unimolecular decomposition, i.e.,

\[
n(t) = n(0) \exp(-kt)
\]

and plots of \(\ln[n(t)/n(0)]\) vs \(t\) were used to determine rate constants from the trajectory calculations. Three of these plots are illustrated in Fig. 7. The microcanonical rate constant is the negative slope of the plot, which is calculated by a linear least-squares regression, along with the standard deviation on the slope and the correlation coefficient. The latter was always greater than 0.99, indicating the fit is good. The rate constants and uncertainties are listed in Table V. The rate constants determined with orthonormal sampling are nearly the same as those determined with microcanonical normal mode sampling. The microcanonical normal mode sampling rate constants for linear and triangular \(A_l_3\) were averaged to approximate the microcanonical rate constant for the complete \(A_l_3\) system.

A comparison of the rate constants in Tables IV and V shows that the average trajectory rate constants are in good agreement with those calculated from the trajectory calculations.
agreement with the OTS/PST and flexible RRKM anharmonic rate constants, when the Al₃ anharmonic density of states is determined by directly solving the phase integral. These OTS/PST and flexible RRKM rate constants are only 25% and 10% larger than the trajectory rate constants at the lowest and highest energy, respectively. The anharmonic rate constants calculated using the Al₃ density of states determined by adiabatic switching are 1.5–2.1 times larger than the trajectory rate constants.

The above analysis shows that the Al₃ density of states and, thus, the model anharmonic unimolecular rate constant are very sensitive to the position of the reactant/product phase space boundary (i.e., transition state structure). If the vibrator transition state model is used to define the phase boundary, the resulting Al₃ anharmonic density of states is very similar to that obtained by adiabatic switching (see Fig. 5). However, if the flexible transition state is used, the density of states is up to 35% larger. Thus, there is interest in determining the best transition state structure for Al₃ dissociation. As pointed out by Bunker,¹⁹,¹⁰² this can be done from the trajectories by ascertaining the largest Al₃+Al separation that is attained without dissociation occurring. Distributions of this separation are plotted in Fig. 8. The maximum separation is 11.73 and 10.16 Å for Eₗ₉ of 0.5 and 1.5 kcal/mol, respectively. As shown in Table II, these separations are intermediate of those for the harmonic vibrator and flexible variational transition state models. The sum of states as a function of the Al₃+Al separation, for Eₗ₉ of 0.5 and 1.5 kcal/mol, is plotted in Fig. 9 for both the vibrator and flexible transition state models. The very shallow minima in the sum of states plots for the flexible model are identified by arrows. One sees that the flexible transition state could be “moved in” from the minimum to the best transition state structure determined dynamically from the trajectories, with only a minor effect on the sum of states. The apparent inability of the flexible model to give the correct transition state structure, for Al₃ dissociation, may result from the neglect of coupling between the transitional and conserved modes by the flexible model.¹⁴⁵ This coupling is an explicit component

---

**TABLE V. Classical trajectory rate constants obtained by microcanonical normal mode sampling about the linear and triangular Al₃ potential minima.**

<table>
<thead>
<tr>
<th>Eₗ₉</th>
<th>Linear</th>
<th>Triangle</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>6.85±0.08</td>
<td>5.22±0.09</td>
<td>5.89±0.77</td>
</tr>
<tr>
<td>0.50</td>
<td>15.56±0.34</td>
<td>12.35±0.17</td>
<td>14.13±1.77</td>
</tr>
<tr>
<td>0.75</td>
<td>26.79±0.12</td>
<td>22.29±0.09</td>
<td>24.55±2.36</td>
</tr>
<tr>
<td>1.00</td>
<td>40.96±0.53</td>
<td>34.49±0.42</td>
<td>37.78±3.71</td>
</tr>
<tr>
<td>1.25</td>
<td>51.50±0.64</td>
<td>51.14±1.38</td>
<td>50.95±1.19</td>
</tr>
<tr>
<td>1.50</td>
<td>72.69±0.45</td>
<td>59.43±0.20</td>
<td>66.19±6.96</td>
</tr>
<tr>
<td>1.75</td>
<td>76.04±0.68</td>
<td>67.60±0.14</td>
<td>71.59±6.13</td>
</tr>
<tr>
<td>2.00</td>
<td>108.57±1.61</td>
<td>81.30±1.84</td>
<td>94.82±15.36</td>
</tr>
</tbody>
</table>

¹Each ensemble contains 200 trajectories unless specified otherwise and the rate constants are obtained by a linear least-squares fitting of the Al₃ population vs time. The uncertainties on the rate constants are given for a 99% confidence level. Energies are in kcal/mol and rate constants in ns⁻¹.

²The ensemble for this energy contains 1000 trajectories.

³Average value and standard deviation of the rate constants for both isomers.

⁴Results in parentheses were obtained by orthant sampling.
of the Hamiltonian used in the trajectory calculations. Since the sum of states for the flexible model is weakly dependent on the Al₂ + Al separation for large values of this separation, it is possible that including this coupling would shift the minimum in the transition state sum of states to the trajectory best transition state.

**B. Product energy partitioning**

The trajectories were analyzed for Al₂ rotational and vibrational energies $E_v$ and $E_r$, and Al₂ + Al relative translational energy $E_t$. Microcanonical normal mode sampling of the linear and triangle minima and orthant sampling gave identical product energy distributions within statistical uncertainties. The product energy distributions given here are total distributions for the microcanonical normal mode sampling ensembles of the linear and triangle minima. Representative distributions of the Al₂ internal energy $E_{int}=E_v + E_r$, and rotational angular momentum $j$ are shown in Fig. 10 for $E_m$ of 0.75 and 1.5 kcal/mol. Since $E_t=E_m-E_{int}$, the distribution for $E_t$ is easily found from that for $E_{int}$. The uncertainties on the distribution are found from the estimated Monte Carlo standard error.$^{170,171}$ The uncertainty in the occurrence number $n_i$ of event $i$ out of a sample of size $n$ is given by

$$\Delta n_i = t_{n-1}(n-n_i)^{1/2},$$

where $t$ is the $t$-student value for the desired confidence level of 99%. Average values of $E_{int}$, $E_v$, and $j$ for the distributions are listed in Table VI. The average relative translational energy is simply $E_t = E_m - E_{int}$. Also listed in this table is the maximum observed value for the Al₂ rotational angular momentum; i.e., $j_{max}$.

Distributions of $E_{int}$, $E_v$, and $j$ calculated with PST and OTS/PST are plotted in Fig. 11. Average values of the distributions are listed in Table VI. A comparison of these plots and average values with the trajectory results shows that both PST and OTS/PST give a good overall agreement with the trajectory calculations. The only significant difference between PST and OTS/PST is for the internal energy distribution $P(E_{int})$ at the highest $E_{int}$ values. The solid lines in Fig. 11 are the distributions predicted by PST. The PST results in Table VI are in accord with the classical equipartition theorem. Also, since the OTS is located at a large Al₂ + Al separation, the OTS/PST average energies are the same as those given by PST.

Engelking has recently proposed a modification of Rice–Ramsperger–Kassel (RRK) theory$^{76-78}$ in its quasiequilibrium theory (QET) form$^{172}$, based on phase space theory$^{85,161-163}$ arguments and microscopic reversibility.$^{25,26}$ His model predicts a relative translational energy release probability density of

$$P(E_t) = \frac{\rho(E_m-E_t)}{\int_0^E \rho(e) e \, de},$$

(46)

If the harmonic energy independent Al₂ density of states is used, $P(E_t)$ becomes $2E_t/E_m^2$ and $E_t$ is $2E_m/3$. When the reaction product is not a diatom but a polyatomic, the average translational energy release becomes $2E_m/(s-1)$, where $s$ is the reactant number of degrees of freedom.$^{25,26}$ A major shortcoming of the Engelking model is that it does not explicitly account for angular momentum. Thus, this model...
TABLE VI. Al3→Al1 + Al product energy and angular momentum distributions from both trajectory and statistical rate theory calculations.

<table>
<thead>
<tr>
<th>$E_{\text{int}}$</th>
<th>$j^d$</th>
<th>$j^\text{max}$</th>
<th>Trajectories</th>
<th>Phase space theory</th>
<th>Orbiting transition state/phase space theory</th>
<th>Engelking model</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.16±0.06</td>
<td>8.5±5.4</td>
<td>22.1</td>
<td>2.0±0.10</td>
<td>8.3±5.4</td>
<td>62.4</td>
</tr>
<tr>
<td>0.50</td>
<td>0.31±0.13</td>
<td>13.1±7.6</td>
<td>30.6</td>
<td>2.0±0.13</td>
<td>11.7±7.6</td>
<td>30.9</td>
</tr>
<tr>
<td>0.75</td>
<td>0.47±0.19</td>
<td>16.3±9.7</td>
<td>37.6</td>
<td>2.0±0.20</td>
<td>14.2±9.2</td>
<td>37.8</td>
</tr>
<tr>
<td>1.00</td>
<td>0.64±0.24</td>
<td>19.6±11.3</td>
<td>43.5</td>
<td>2.0±0.31</td>
<td>16.5±10.7</td>
<td>44.1</td>
</tr>
<tr>
<td>1.25</td>
<td>0.80±0.32</td>
<td>20.6±12.3</td>
<td>47.5</td>
<td>2.0±0.51</td>
<td>18.5±12.0</td>
<td>49.3</td>
</tr>
<tr>
<td>1.50</td>
<td>0.94±0.38</td>
<td>23.3±13.6</td>
<td>53.4</td>
<td>2.0±0.56</td>
<td>20.2±13.2</td>
<td>54.0</td>
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<td>25.2±14.8</td>
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<td>58.3</td>
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<td>26.2±15.0</td>
<td>60.1</td>
<td>2.0±0.62</td>
<td>23.3±15.2</td>
<td>62.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.15±0.07</td>
<td>8.3±5.4</td>
<td>22.1</td>
<td>2.0±0.10</td>
<td>8.3±5.4</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.30±0.13</td>
<td>11.7±7.6</td>
<td>32.1</td>
<td>2.0±0.13</td>
<td>11.7±7.6</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.45±0.20</td>
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<td>38.2</td>
<td>2.0±0.20</td>
<td>14.3±9.3</td>
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<tr>
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<td>1.00</td>
<td>0.60±0.26</td>
<td>16.5±10.7</td>
<td>44.1</td>
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<tr>
<td></td>
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<td>0.75±0.33</td>
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<tr>
<td></td>
<td>1.75</td>
<td>1.05±0.46</td>
<td>21.8±14.2</td>
<td>58.3</td>
<td>2.0±0.46</td>
<td>21.8±14.2</td>
</tr>
<tr>
<td></td>
<td>2.00</td>
<td>1.20±0.52</td>
<td>23.3±15.2</td>
<td>62.4</td>
<td>2.0±0.52</td>
<td>23.3±15.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Energies are in kcal/mol and angular momenta in $\hbar$. Listed uncertainties are the standard deviations of the distributions. Averages and standard deviations for the statistical rate theory distributions are found by Gaussian quadrature.

Al1 vibrational/rotational energy.

Al2 vibrational energy.

Al2 maximum angular momentum. Calculated from Eq. (A6) for OTS/PST.

(1) The classical trajectory unimolecular lifetime distributions calculated for Al3 dissociation vs $E_{\text{int}}$ agree with the random lifetime distribution of RRKM theory, which indicates Al3 is an intrinsic RRKM molecule.

(2) Flexible and vibrator variational RRKM theory, phase space theory (PST), and the orbiting transition state model of phase space theory (OTS/PST) are used to calculate the sum of states for the Al3→Al1 + Al1 transition state. Flexible RRKM theory, PST and OTS/PST give nearly identical transition state sums of state. The vibrator RRKM model gives a sum of states which is 40% and 10% larger at the lowest and highest energy, respectively.

(3) At low energies, where the flexible variational transition state becomes very loose, flexible variational RRKM theory approaches PST. OTS/PST is a variational unimolecular rate theory for isotropic long-range potentials, with orbital angular momentum treated as an adiabatic degree of freedom at the transition state.

(4) Adiabatic switching gives an Al3 anharmonic density of states which is 2.5 larger than the harmonic density at the unimolecular threshold and 2.9 larger with 2.0 kcal/mol excess energy above the threshold. The Al3 anharmonic density, determined by directly solving the phase integral, is sensitive to the position of the reactant/product phase space boundary. If it is placed at the variational vibrator transition state, the resulting density of states is nearly the same as that found by adiabatic switching. However, if the phase space boundary is placed at the much looser flexible variational transition state.

VI. SUMMARY

The studies presented in this paper for Al3→Al1 + Al dissociation with 0.25–2.0 kcal/mol excess energy $E_{\text{int}}$ above the classical threshold leads to the following conclusions:

the resulting Al₃ density becomes significantly larger than that found by adiabatic switching. At Eₐ₈ = 2.0 kcal/mol, it is 35% larger.

(5) If one uses the Al₃ anharmonic density of states found by directly solving the phase space integral, with the flexible transition state phase space boundary, the OTS/PST and flexible RRKM rate constants are in good agreement with the trajectory results. The OTS/PST and flexible RRKM rate constants are 25% and 10% larger at the lowest and highest excess energy, respectively.

(6) The dynamical bottleneck, separating the reactant Al₃ from the Al₂ + Al products, is determined from the trajectories and found to have a Al₂ + Al center-of-mass separation smaller than that for the orbiting transition state or the flexible variational transition state and larger than that for the vibrational variational transition state. The sum of states for the flexible variational transition state is insensitive to the Al₂ + Al center-of-mass separation, for large separations, and, if coupling was included between the transitional and conserved modes in the Hamiltonian for the flexible model, this modified flexible model might give a transition state structure in accord with the trajectory dynamical bottleneck. The uncertainty in the position of the phase space boundary between reactants and products leads to an ambiguity when determining the Al₃ anharmonic density of states by directly solving the Al₃ phase space integral.

(7) Both PST and OTS/PST give near quantitative agreement with the Al₂ + Al product energy partitioning determined from the trajectory calculations. The Engeling model gives product energy distributions qualitatively different from the trajectory results.

In the trajectory calculations reported here an average potential energy surface is used to represent the low-lying electronic states for Al₃→Al₂ + Al dissociation. In particular, there are two low-lying Al₃ electronic states, 3Π_u and 3Σ−g, which are separated by no more than 200 cm⁻¹. If both of these states are coupled to the Al₂ dissociation process, the trajectory calculations reported here indicate that each should be formed with a rate in accord with RRKM theory. However, the rates to form the two states will be slightly different since their energies are slightly different. Similarly, product energy distributions, for both the 3Π_u and 3Σ−g electronic states of Al₂, are expected to be in accord with PST and OTS/PST. On the other hand, if transitions between the Al₃ electronic states are infrequent and nonstatistical, the model used here, of an average potential energy surface, could be inappropriate for describing the Al₃→Al₂ + Al dynamics. To answer this question more detailed information is needed about the transitions between the electronic states than is currently available.

ACKNOWLEDGMENTS

This research was supported by Donors of the Petroleum Research Fund, administered by the American Chemical Society, the Institute of Manufacturing Research of Wayne State University, and the National Science Foundation. G.H.P. would like to thank Haobin Wang for useful discussions throughout this work. W.L.H. would like to thank Petra van Koppen for insights concerning OTS/PST.

APPENDIX A: PERSISTENT AND OTS/PST CALCULATIONS FOR Al₃→Al₂+Al

With total angular momentum J=0, two significant simplifications arise when applying PST to Al₃ dissociation. The product rotational angular momentum and rotational energy, denoted j and E_r, respectively, are those for a diatom; i.e.,

\[ E_r = B_r j^2, \]

where \( B_r \) is the rotational constant. Since \( j = l \) double integrals over \( j \) and \( l \) can be replaced by a single integral over either \( j \) or \( l \), so that the rotational-orbital sum of states reduces to

\[ \Gamma^\pm (E_r, J) = \int \Gamma^\pm (E_r, j) dj, \]

where \( \Gamma^\pm (E_r, j) \) is the sum of product rotational states at rotational energy \( E_r \) and rotational angular momentum \( j \). For atom-rigid rotor pairs, \( E_r \) and \( j \) are related by Eq. (A1). \( \Gamma^\pm (E_r, j) \) is then the rotational degeneracy of the rigid rotor, which is unity for the atom–diatom case. Thus,

\[ \Gamma^\pm (E_r, J) = \int_0^{j_{\text{max}}(E_r)} \Gamma^\pm (E_r, j) dj \]

\[ = \int_0^{j_{\text{max}}(E_r)} 1 \cdot dj \]

\[ = j_{\text{max}}(E_r). \]

The PST rate constant is found by inserting Eq. (A3) into Eq. (28) and, following Klots, the result can be expressed as Eq. (29).

In OTS/PST the value for \( j_{\text{max}}(E_r) \) in Eq. (A3) is different, since the available translational–rotational energy \( E_{\text{tr}} \) is evaluated at the centrifugal barrier instead of the asymptotic product limit of PST. For the long-range isotropic potential in Eq. (30), the height of the centrifugal barrier, with respect to the asymptotic potential limit, is given by

\[ \epsilon^= \frac{j^2(n(n-2))}{\Lambda}, \]

where

\[ \Lambda = \frac{2(n \mu)^{n(n-2)} c^{2(n-2)}}{n-2} \]

and \( \epsilon^= \) represents the minimum product relative translational energy for a particular \( I \). For \( j = l \), \( I \) in Eq. (A4) can be replaced with \( j \) and \( j_{\text{max}}(E_r) \) can be found from

\[ E_r + \epsilon^= = B_r j^2 + \frac{j^2(n(n-2))}{\Lambda} \approx E_{\text{tr}}. \]

The resulting \( j_{\text{max}}(E_r) \) gives \( \Gamma^\pm (E_r, J) \) in Eq. (A3), which is inserted into Eq. (28) to give the OTS/PST microcanonical rate constant.

According to PST, the probability of forming products with given properties is proportional to the total phase space volume accessible to the system, whose differential form is

\[ \rho^\pm (E_w - E_t - E_r) \rho^\pm (E_r, j) dj \ dE_r \ dE_t, \]
where \( \rho_\delta^E(E) \) is the product vibrational density of states and \( \rho_\delta^J(E_r,j) \) is the product rotational density of states, given by

\[
\rho_\delta^J(E_r,j) = \frac{\partial}{\partial E_r} \Gamma^J(E_r,j). \tag{A8}
\]

Since \( j=1 \), differentiation over \( j \) in Eq. (A7) has been replaced by a single differentiation over \( j \). The integral form of Eq. (A7) can be rewritten, through use of Eqs. (A2) and (A8), as a single integral over \( E_\nu \), as given in Eq. (28).

To find the product internal energy distribution, one needs to evaluate the translational energy release probability density, which is proportional to the integral form of Eq. (A7) at fixed \( E_r \); i.e.,

\[
P_{E_r}(E_\nu) \propto \int \rho_\delta^J(E_\nu - E_r - E_r) \rho_\delta^J(E_r,j) dj \ de_r. \tag{A9}
\]

Replacing the convolution over \( j \) by a convolution over \( E_r \), using the Jacobian of the transformation of Eq. (A1), yields the familiar result by Klotz in Eq. (33). Similarly, the product rotational angular momentum probability density is proportional to the integral form of Eq. (A7) at fixed \( j \), which yields Eq. (34).

In OTS/PST the integral boundaries for the product energy distributions are evaluated at the centrifugal barrier. The boundaries of \( j(1) \) in Eq. (A10) are given by \( \delta^2 \approx E_\nu \) [see Eq. (A6)]. The boundaries of \( E_\nu \), in Eq. (34) are given by \( \delta \approx E_\nu \leq E_\nu - B_j j^2 \). These boundaries have the effect of adding \( \delta \) to product translation.

**APPENDIX B: RELATIONSHIP BETWEEN PST, OTS/PST, AND THE FLEXIBLE TRANSITION STATE MODEL OF RRKM THEORY**

The orbiting transition state model of phase space theory and the flexible variational transition state model of RRKM theory are both based on the separable long-range product Hamiltonian

\[
H = H_\nu + H_\nu + T_r + T_r + \frac{l^2}{2 \mu r^2} + E_r + V, \tag{B1}
\]

where the \( H_\nu \)'s and the \( T_r \)'s are the vibrational Hamiltonians and rotational kinetic energies of the reaction fragments, \( l \) is the orbital angular momentum, \( \mu \) is the reduced mass of the fragments, \( r \) their center-of-mass separation, \( E_r \) is the relative translational energy projected on the fragments center-of-mass separation, and \( V \) is the intermolecular potential. The unimolecular system’s total angular momentum is the vector sum of the rotational angular momenta \( J_1 \) and \( J_2 \) for the two fragments and the orbital angular momentum \( I \). OTS/PST are derived for a long-range isotropic potential, so that \( V \) only depends on \( r \). While applications of the flexible model have been for anisotropic potentials, it is important to compare the OTS/PST model and the flexible RRKM model for the limiting case of an isotropic potential.

OTS/PST can be viewed as a variational unimolecular rate theory which minimizes the reaction flux vs \( E, J, \) and \( l \). For an isotropic long-range potential, the resulting transition state will be at the centrifugal barrier. From Eq. (28) the transition state sum of states for a particular \( E, J, \) and \( l \) is then

\[
N^J(E, J, l) = \int \rho_\delta^J(E_\nu - E_r) \int \Gamma^J(E_r,j) dj \ de_r. \tag{B2}
\]

where \( \delta \) is the height of the centrifugal barrier with respect to the asymptotic limit, \( \Gamma^J(E_r,j) \) is the rotational sum of states at the orbiting transition state and, for the general case, is related to \( \Gamma^J(E_\nu, J) \) in Eq. (28) by

\[
\Gamma^J(E_\nu, J) = \int \Gamma^J(E_r,j) dj \ dl. \tag{B3}
\]

Thus, \( N^J(E, J) \) in OTS/PST is simply the integral of \( N^J(E, J, l) \) in Eq. (B2) over \( l \); i.e.,

\[
N^J(E, J) = \int N^J(E, J, l) dl. \tag{B4}
\]

In contrast to OTS/PST which locates a transition state and calculates the unimolecular rate constants as a function of \( E, J, \) and \( l \), the flexible model calculates a variational unimolecular rate constant only as a function of \( E \) and \( J \). Thus, following Eq. (20), the transition state sum of states for the flexible model is

\[
N(E, J) = \int [V(r) - E_\nu - \delta_\nu] N_{\nu}(\delta_\nu) d\delta_\nu. \tag{B5}
\]

The sum of states \( N_{\nu}(\delta_\nu) \) includes contributions for all possible values of orbital angular momentum \( l \), so that the variational transition state of the flexible model is the best compromise of all variational transition states as a function of \( E, J, \) and \( l \). As a result, for an isotropic intermolecular potential, OTS/PST gives a variational \( k(E, J) \) less than or equal to that of flexible variational RRKM theory. This relationship is similar to that between \( k(E, J) \) calculated for the harmonic vibrator variational transition state model with the quantum number treated as either active or adiabatic.

It is interesting to note that the flexible variational RRKM model approaches PST as the energy is lowered and the separation \( r^{\delta} \) between the product fragments becomes very large at the variational transition state. This is because the \( l^2/2 \mu r^2 \) and \( V \) terms in Eq. (B1) become negligible, so that the flexible Hamiltonian becomes

\[
H = H_\nu + H_\nu + T_r + T_r + E_r \tag{B6}
\]

which is the Hamiltonian of PST. PST and the flexible variational RRKM model use different sets of conjugate coordinates and momenta to determine phase space volumes for the degrees of freedom that are treated classically. However, both models use the same conservation laws, i.e., total energy and that of angular momentum, and when the flexible
Hamiltonian approaches that of PST, the flexible variational RRKM rate constant approaches that of PST.

To illustrate the latter point, consider the flexible variational RRKM rate constant for $\text{Al}_2$ dissociation. The transition state potential of the product diatom and the magnitude of the interaction potential $V_0(r)$ in Eq. (24) also decreases, approaching zero. The sum of states then becomes $(E_{\text{TR}}/B_j)^{1/2}$, where $E_{\text{TR}}$ is the transition state energy and $B_j$ is the diatom rotational constant. Inserting this expression into Eq. (20) yields the PST rate constant in Eq. (29). For $E_{\text{ad}}=0.25$ kcal/mol, the PST and flexible RRKM rate constants are nearly the same and the flexible transition state has the properties $r^*=19.87 \, \text{Å}, V_0(\rho^*)=0.0033$ kcal/mol, and $I(\rho^*)/0.987$ times the diatom moment of inertia. For $E_{\text{ad}}=2.0$ kcal/mol, the difference between the PST and flexible RRKM rate constants is slightly larger and the flexible transition state has the properties $r^*=13.84 \, \text{Å}, V_0(\rho^*)=0.0035$ kcal/mol, and $I(\rho^*)/0.974$ times the diatom moment of inertia.


12 J. Koutecky and P. Fantucci, Chem. Rev. 86, 539 (1986), and references therein.


14 The issue Z. Phys. D 3 (1988) is also mostly devoted to metal cluster studies.

15 W. A. de Heer, Rev. Mod. Phys. 65, 611 (1993), and references therein.


151 See discussion in Refs. 131 and 145.
152 The transitional modes are the intramolecular modes whose nature changes drastically in the course of the dissociation reaction; i.e., they become translations and rotations in the product region, see Y. N. Lin and B. S. Rabbinovitch, J. Phys. Chem. 74, 3151 (1970).
165 Klots, Ref. 83, has pointed out that typically 2S equals R−1, where R is the total number of rotational degrees of freedom. For Al3 dissociation with J=0 and therefore confined to a plane, there is only one rotational degree of freedom, but S=1/2.