Phase Space Analysis of Formaldehyde Dissociation Branching and Comparison with Quasiclassical Trajectory Calculations[†]

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We investigate the dependence of the branching ratio of formaldehyde dissociation to molecular and radical products on the total energy and angular momentum and the HCO rotational state distributions by using a combination of transition state/Rice−Ramsperger−Kassel−Marcus theory and phase space theory. Comparisons are made with recent quasiclassical trajectory (QCT) calculations [Farnum, J. D.; Zhang, X.; Bowman, J. M. *J. Chem. Phys*. **2007**, *126*, 134305]. The combined phase-space analysis is in semiquantitative agreement with the QCT results for the rotational distributions of HCO but is only in qualitative agreement for the branching ratio. Nevertheless, that level of agreement serves to provide insight into the QCT results, which showed suppression of the radical channel with increasing total angular momentum for a fixed total energy.

I. Introduction

The photodissociation dynamics of formaldehyde has been the focus of experimental[1−10] and theoretical work[11−23] for more than 20 years. A recent resurgence of interest has emerged because of new experiments[7−10] and dynamics calculations[7,19−23] done with an ab initio-based full-dimensional global potential energy surface[18] (PES) that describes both the molecular and the radical channels, $H_2 + CO$ and $H + HCO$, respectively.

The reaction proceeds through three reaction channels

$$(1)\ H_2CO \xrightarrow{TS} H_2 + CO$$

$$(2)\ H_2CO \rightarrow H + HCO$$

$$(3)\ H_2CO \xrightarrow{\text{“roaming”}} H_2 + CO$$

Channel (1) passes through the traditional transition state (TS), and channel (3) is the recently described “roaming” channel[7,22,23] to molecular dissociation in which the molecule bypasses the molecular TS and produces molecular products through a frustrated radical dissociation event followed by abstraction of the hydrogen from the HCO fragment.

Quasiclassical trajectory (QCT) studies on this PES have elucidated the dissociation reaction mechanisms and, specifically, its branching ratio. Previous theoretical investigations of the dissociation dynamics have shown that the radical channel branching ratio increases with increasing energy;[19,20] however, these calculations were done for zero total angular momentum (J). In very recent work,[23] QCT calculations were done for a large range of J, and one result of these studies was the finding of suppression of the radical channel with increasing rotational excitation at fixed total energy. To further investigate the dissociation dynamics and especially to provide additional insight into the QCT results, we present a phase space analysis of the dissociation in this paper. We restrict this analysis to channels (1) and (2) because at this time we are not aware of a phase space approach that is applicable to the roaming channel (3). However, we do speculate on how this channel might qualitatively affect the present analysis.

A variety of phase space/statistical techniques have been developed for different kinds of reactions.[24−30] Perhaps the most widely used approach is the Rice−Ramsperger−Kassel−Marcus (RRKM) theory,[28,29] which sums the available phase space of a reaction at a well-defined, “tight” TS, generally a saddle-point, at a fixed total energy and angular momentum. The molecular dissociation channel of formaldehyde has a distinct saddle point TS and is well suited for the application of RRKM theory. However, the radical channel to dissociation has no barrier and thus no distinct TS. Phase space theory (PST)[25−27] is a technique that is specifically designed for this case. PST focuses on the phase space available to the products, with particular consideration of angular momentum conservation, and the role of centrifugal potentials. For the present case of formaldehyde dissociation we use RRKM theory to analyze the accessible phase space of the molecular channel because a “tight” saddle point TS is present on the potential surface for that channel. We use PST to analyze the accessible phase space of the radical channel because no saddle point exists on the potential surface for this channel. We note that more sophisticated “statistical” treatments are possible for the radical channel;[31] however, these are beyond the scope of the present goal, which is a qualitative understanding and hopefully semiquantitative agreement with the QCT calculations.

In this paper we focus on the rotational distribution of the HCO product, the product branching ratio, and their dependencies on the total energy and total angular momentum, and we compare the results of this combined phase space approach with previous QCT calculations. In the next section we describe the details of the calculations and some relevant properties of the potential. Following that, we present our results and discussion in section III and summarize and state our conclusions in section IV.

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II. Calculations

A postulate of PST applied to a unimolecular dissociation reaction is that the branching ratio of reaction products is proportional to the ratio of volumes of phase space available to the system in each pathway. Taken quantum mechanically, the phase space becomes a discrete set of states, and integrating the volume simplifies to summing the number of possible states that obey the restrictions of energy and angular momentum conservation. Mathematically, the branching ratio of channel i takes the form

$$P_i(E,J) = \frac{N_{E,J,i}}{N_{E,J}} \tag{1}$$

where $N_{E,J,i}$ equals the number of states satisfying the constraints of energy and angular momentum conservation as well as having the quantum characteristics of channel i, and $N_{E,J}$ equals the total number of states available within the energy and angular momentum constraints.

For the present application to formaldehyde dissociation, the set of accessible quantum states can be split into the set of accessible states at the TS for molecular dissociation and the set of states accessible to the radical dissociation products at the centrifugal barrier. Because the molecular channel has a tight, well-defined TS, the number of states for the molecular channel is obtained with a straightforward RRKM formulation. The relevant quantum numbers are the real-frequency vibrational modes and J and K rotational quantum numbers, assuming that the molecule is a symmetric top (which is an excellent approximation). The summation of states for a fixed total energy E and total angular momentum J is given by eq 2

$$N_{E,J,\mathrm{molecular}} = \sum_{\nu_i,K} \Theta[E - E^{\mathrm{TS}}(\nu_i,J,K) - E_{\mathrm{TS}}] \tag{2}$$

where ν_i represents the five vibrational quantum numbers, E is the total energy of the system measured relative to the zero-point energy of equilibrium formaldehyde, E_{TS} is the height of the TS barrier measured relative to the formaldehyde zero-point, and E^{TS} is the vibrational and rotational energy of the quantum state relative to the top of the TS barrier. Θ denotes the unit step function that is equal to one when the quantity inside the brackets is positive and is zero when the quantity is negative. What is sometimes termed "fixed" energy in the literature consists of the zero-point energies of the vibrations at the TS and the TS barrier height. The remaining energy is available for vibrational and rotational excitation. The set of possible combinations of quantum excitations that have energy at or below the limit of available energy represents the available phase space for molecular dissociation. The step function counts a state only if the energy of that state is at or below the total energy. Rigid-rotor and harmonic-oscillator models for the internal energy of the molecule are typically used, and we do so here. The rigid-rotor model is satisfactory if the TS is sufficiently tight and if there is a relatively low level of excess energy. Similarly, if the vibrational modes are not highly excited, then the harmonic-oscillator model is a good approximation to the energy of the vibrational excitations.

The phase space for the radical channel is more difficult to define because it is a barrierless reaction and has no clear TS from the PES. However, PST can treat reactions like the radical dissociation, which have very "loose" TSs. As the molecule fragments, centrifugal barriers develop, depending on angular momentum constraints. Variational PST identifies the barrier as a local maximum on the effective potential, that is, the sum of the electronic potential plus the centrifugal potential, which is the best place to define the TS and sum the available states. Even though this barrier is not a real potential energy element, the height of the barrier with respect to the asymptotic limit of the fragment energy is equal to the minimum amount of energy that must necessarily be in relative translational energy for fragmentation to classically occur.

In PST, the relevant quantum numbers for the radical channel are the quantum numbers of the fragments. Therefore, the quantum numbers are the three vibrational states of the HCO fragment (again, assumed to be adequately described by normal-mode harmonic-oscillators), the j and k rotational quantum numbers of HCO (assuming that it is a symmetric top, which again is an excellent approximation), and the relative angular momentum between the HCO and H fragments (l). The summation of states can be given in very compact form by eq 3[30]

$$N_{E,J,\mathrm{radical}} = \sum_{\nu_i,j,k,\ell} \Theta[E - E_{\mathrm{HCO}}(\nu_i,j,k) - E_{\mathrm{CB}}(l) - E_{\mathrm{diss}}]\Delta(J,j,l) \tag{3}$$

where E is again the total energy measured relative to the formaldehyde zero-point energy, E_{HCO} represents the energy of the HCO product, E_{CB} is the centrifugal barrier term, and E_{diss} is the dissociation energy from formaldehyde zero-point energy to the H + HCO (eq) energy. The Δ term takes into account restrictions on the related rotational quantum numbers. In this formulation, the centrifugal barrier is taken as the difference between the barrier peak and the asymptotic energy of the dissociated fragments at equilibrium. The relative angular momentum determines the height of the centrifugal barrier E_{CB}. Because the centrifugal barrier changes, the set of quantum states includes the range of possible l values that allow dissociation. l and j are related, by conservation of angular momentum, to the angular momentum quantum number of the parent formaldehyde molecule, J. Both classically and quantum mechanically, $\vec{J} = \vec{j} + l$, and quantum mechanically, the triangle inequality relates the quantities, $|J - j| \leq l \leq |J + j|$. In the summation of states, the Δ-function enforces the triangle inequality by taking the value of unity only at allowed values of J, j, and l and takes the value of zero everywhere else.

The effective potential is the sum of the electronic potential energy and the quantity $l^2/2\mu r^2$, where l is the relative (orbital) angular momentum quantum number, μ is the reduced mass of the fragments, and r is the separation of the dissociating fragments. The potential energy for the radical dissociation reaction is taken to be the minimum energy pathway from the H_2CO minimum to the separated radical fragments at their respective minima. Stretching one of the CH bonds of formaldehyde at equilibrium to dissociation length while freezing the other formaldehyde coordinates approximates the minimum energy path. (As discussed previously,[23] the difference in energy due to relaxation of the HCO fragment is negligible.) The combined potential and centrifugal components produce a centrifugal barrier. In addition to the energy required for radical dissociation (to equilibrium), the height of the centrifugal barrier with respect to infinitely separated radical fragments must be known. This energy is measured relative to the dissociation energy.

All calculations here use the PES of ref 12, which has been used in extensive QCT calculations, including the very recent ones examining the effect of rotational distributions of HCO

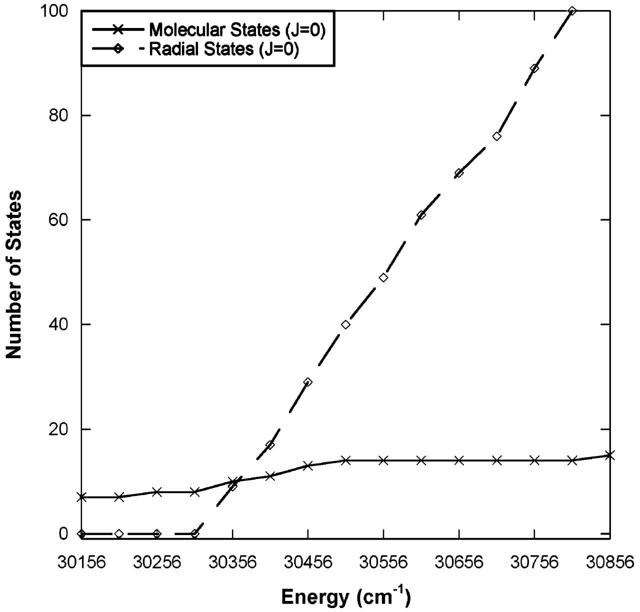

Figure 1. Number of states available to the radical and molecular channels for a range of energies relative to the harmonic zero-point energy of H_2CO for total angular momentum $J = 0$. The threshold to molecular dissociation on the PES is 28 486 cm^{-1} with harmonic zero-point correction, and the threshold to radical dissociation is 30 330 cm^{-1}.

and the channel branching ratio on the total energy and angular momentum.[23] For the radical channel, we performed an accurate third-order fit to a set of barrier heights and l values, and this allows for efficient calculation of the total fixed energy with varying l. On the basis of this fit, the centrifugal barrier is given by eq 4

$$E_{CB}(l) = 0.0077l^3 + 0.6743l^2 - 4.9159l - 2.7642 \quad (4)$$

with the resulting centrifugal barrier in units of cm^{-1}. Finally, the branching ratio for the radical channel is given by eq 5.

$$P_{E,J,\mathrm{radical}} = \frac{N_{E,J,\mathrm{radical}}}{N_{E,J,\mathrm{radical}} + N_{E,J,\mathrm{molecular}}} \quad (5)$$

III. Results and Discussion

In this section we present the results of the “hybrid phase-space” analysis of the molecular and radical dissociation channels in H_2CO. We begin with the $J = 0$ case to establish a “baseline” for consideration of $J > 0$ and the changes caused by this rotational excitation of the formaldehyde molecule.

The relevant (classical) threshold energies for the dissociation are the energy of the (saddle point) TS to molecular dissociation (28 486 cm^{-1}) and the energy required for radical dissociation (30 330 cm^{-1}). Note that these energies include harmonic zero-point energies relative to the H_2CO zero-point energy, and the term “classical” is used to indicate the absence of tunneling but the inclusion of the zero-point energy. Thus, the threshold for dissociation to molecular products is below the one for radical products by 1844 cm^{-1}. Figure 1 shows the number of available states for each pathway in the case of $J = 0$. The molecular channel opens first (far below the range of the plot), but as soon as the energy surpasses the 30 330 cm^{-1} threshold, the radical channel quickly overtakes the molecular channel. The radical channel has a greater increase in states than the molecular channel because the radical channel has the flexibility to support internal rotation while maintaining a zero total angular momentum, and the molecular channel does not.

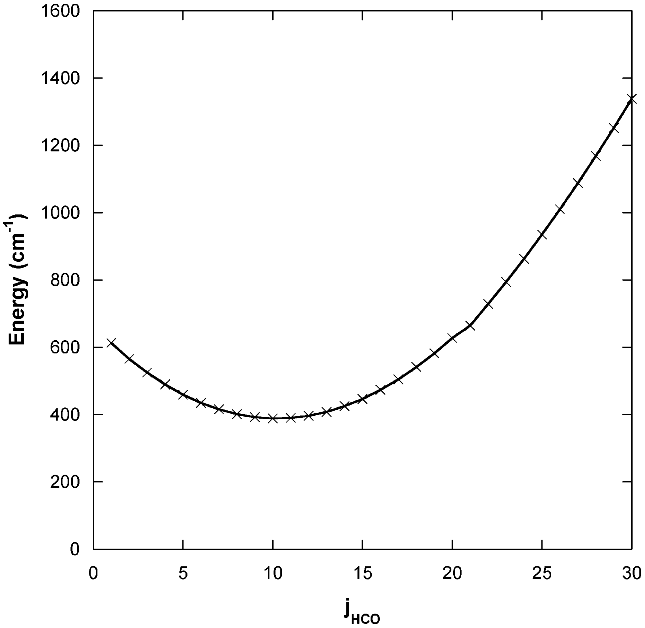

Figure 2. The sum of the HCO rotational energy plus the centrifugal barrier vs j_{HCO} for total H_2CO angular momentum $J = 30$. The minimum energy occurs when $j_{HCO} + l = J$, as discussed in the text.

Once the parent formaldehyde molecule is given rotational excitation, the phase space for both the molecular and the radical channels changes according to eqs 2 and 3, respectively. It is clear from these expressions that the thresholds for both channels shift to higher energy with increasing J. The molecular channel shifts more than the radical channel with increasing rotation, and eventually, the thresholds reverse order at the switching value J_{SW}. However, as we shall see below, the major effect on the branching ratio before the switching value is reached is the shift in the threshold for the radical channel.

To understand this, recall that the radical channel is closed classically when the relative H + HCO translational energy is below the centrifugal barrier on the effective potential. When J is nonzero, the j and l vectors are no longer restricted to be equal and opposite but are constrained by the triangle inequality $|J - j| \leq l \leq |J + j|$. Because particular values of J and j allow for a range of possible l values (and hence centrifugal barriers), there is a “tradeoff” in the centrifugal barrier and translational energy. The largest value of the argument in the step function in eq 3 occurs when the sum $E_{\mathrm{radical}}(\nu_i,j,k) + E_{CB}(l)$ is a minimum and is subject to the triangle inequality constraint. Clearly, the minimum HCO energy occurs for the zero-point state and when $k = 0$, and thus it is only necessary to focus on the minimization with respect to j and l. It is easy to show that the minimization with respect to these angular momenta for fixed J occurs when the J and j vectors are aligned. To make this quantitative, we plot this sum in Figure 2 for $J = 30$ as a function of j. As seen, the minimum occurs at $j = 10$ (implying $l = 20$), where this energy equals 388 cm^{-1}. Thus, according to PST, H_2CO dissociation to H + HCO with $J = 30$ has a (classical) threshold of 388 cm^{-1} above the $J = 0$ threshold of 30 330 cm^{-1}.

It is also straightforward to derive an approximate analytical expression for the threshold energy by noting that the classical expression for the HCO rotational energy is given by Bj^2 (for $k = 0$) and approximating the centrifugal barrier fit (eq 4) by

Cl^2. Thus the rotational energy barrier is given approximately by eq 6.

$$E_{\mathrm{rot}} = Bj^2 + Cl^2 \qquad (6)$$

Minimizing this is trivial, and substituting the minimum value for l at a particular J and j, recall that $l = J - j$ is the minimum value of l, returns the threshold energy for channel 2, as shown in eq 7;

$$\mathrm{E}_{0,2}(J) \approx \mathrm{E}_{0,2}(J = 0) + \frac{BC}{B + C} J^2 \qquad (7)$$

The constants from the present investigation, $B = 1.44$ cm^{-1} and the second-order coefficient in the barrier fit, $C = 0.67$ cm^{-1}, give a coefficient of 0.457 cm^{-1} to the J^2 term, which agrees well with Troe's recently published[31] value of 0.43 cm^{-1}. The present coefficient gives an approximate energy threshold of 412 cm^{-1} for $J = 30$, which is in good agreement with the numerical value of 388 cm^{-1}.

The increased energy requirements of the radical channel due to rotation result in suppression of the radical channel with increasing initial rotational excitation at a fixed energy. Figure 3 shows the branching ratios of the radical channel for a set of J values. The upper plot shows the results of the recent QCT calculations,[24] and the lower panel shows the results of the present combined phase space analysis. The phase space results differ significantly from the QCT results mainly by rising much more rapidly with E for fixed J. However, the present analysis, based on shifts in the molecular and radical thresholds with J, does offer a qualitative explanation of the QCT results, which were not entirely transparent. Note that the phase space threshold agrees with the QCT ones to within roughly 50 cm^{-1}.

There are several possible explanations for the error in the phase space results. One is the effect of the roaming channel (3). As noted in the introduction, this channel is a "self-reaction" of the incipient radicals to form the molecular products. Thus, this channel depletes the flux leading to radicals. Because this channel is not accounted for in the present phase space analysis, its depletion effect is missing in that analysis. Another possible explanation is that the QCT radical flux samples more of the PES as the energy increases above the threshold and deviates from the minimum energy bond-breaking path used in the phase space analysis. Indeed, inspection of individual QCT trajectories leading to radical dissociation reveals a significant number that do not follow the minimum energy path (MEP). Because the PES, in general, has anisotropy, deviations from the MEP result in centrifugal barriers that differ from the MEP barrier.

In addition to suppression of the radical channel branching ratio, the previous QCT calculations found that rotational excitation of formaldehyde causes suppression of the low j values of HCO and an enhancement of the higher j-values. Figure 4 shows the rotational distribution of the HCO fragment at a total energy of 31 656 cm^{-1}, relative to the H_2CO zero-point energy, for $J = 0$, 10, 20, and 30. The upper plot shows the previous QCT results, and the bottom one is the predictions of PST. Note that these distributions are normalized to sum to unity. In this comparison, PST is in very good agreement with the QCT results and also offers insight into the dynamics. Figure 2 helps to explain the effects of J excitation of H_2CO on the j distribution. As J increases, the minimum energy threshold shifts toward higher values of j, and low values of j lead to an increase in the rotational energy. This is because the energy of rotational excitation depends upon the square of the angular momentum. To minimize the energy, both j and l must be kept small. When J increases, both j and l have to increase to keep the energy at a minimum. Therefore, increasing J suppresses small j values and enhances higher j values. It should be noted that the PST results differ slightly from the QCT results in that they overemphasize the high j_{HCO} values. This is a phenomenon attributed to the anisotropy of the potential for which PST does not account. Dissociation trajectories with a high level of rotational excitation in the HCO fragment will sample areas of the PES that differ from the MEP during dissociation. Troe observes the phenomenon in his study of n-propylbenzene.[32]

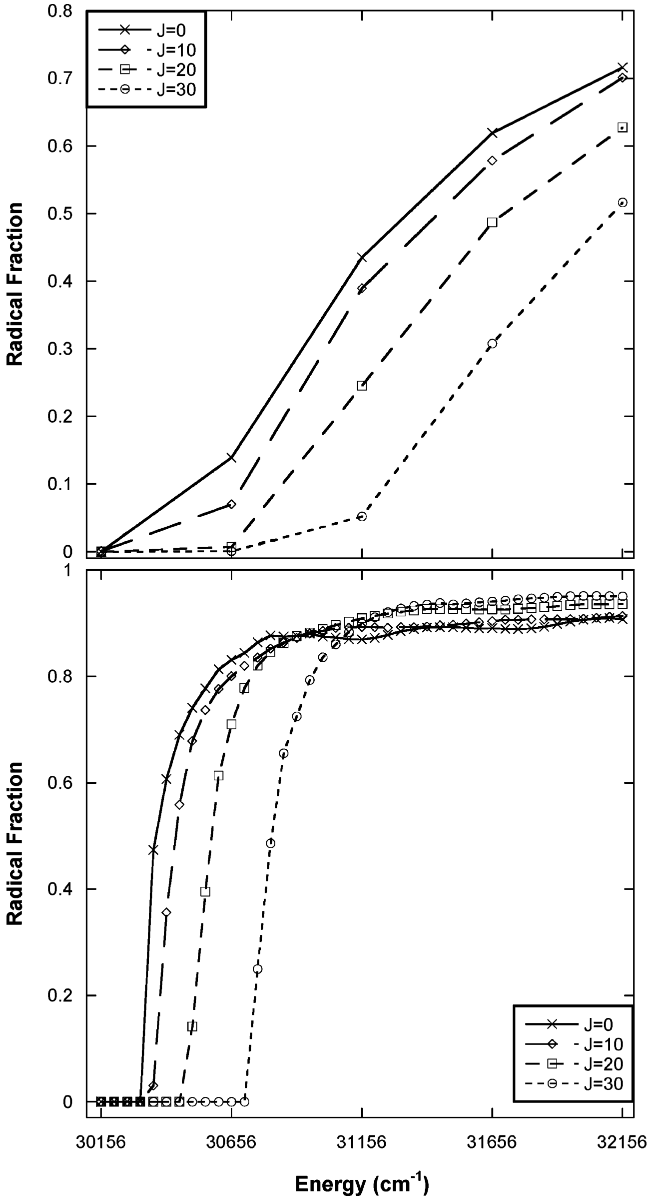

Figure 3. Radical channel branching ratio from quasiclassical trajectory (upper panel) and present statistical (lower panel) calculations vs total energy relative to the harmonic zero-point energy of formaldehyde for total angular momentum $J = 0$, 10, 20, and 30.

IV. Summary and Conclusions

We presented a combined RRKM−PST analysis of the unimolecular dissociation of formaldehyde to form molecular and radical products, $H_2 + CO$ and $H + HCO$, respectively, using a global PES. RRKM theory was used to describe the molecular channel, which has a tight saddle point TS, and PST was used to describe the radical channel, which does not have a potential barrier. The dependences of the branching ratio to

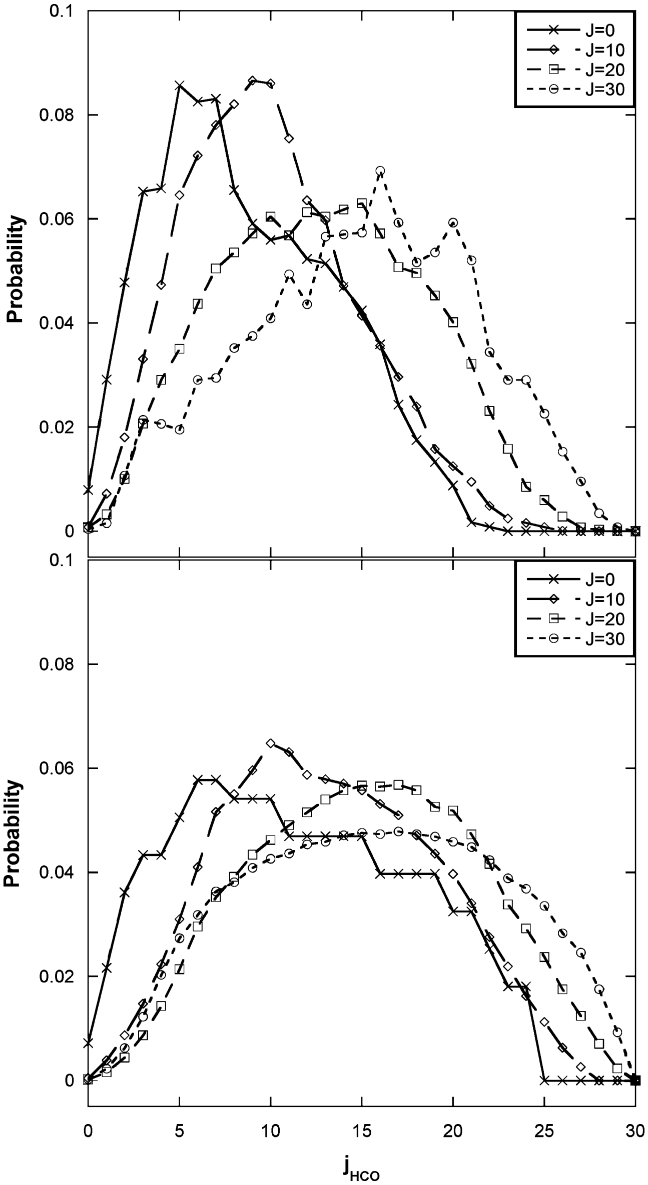

Figure 4. Rotational distributions of the HCO fragment from radical dissociation for total energy of 31 656 cm^{-1} relative to the harmonic zero-point energy of formaldehyde. All curves are normalized to unit area. QCT results are in the top panel, and the present phase space results are in the bottom panel.

form the radical products and of the HCO rotational distribution on the total energy *(E)* and angular momentum (*J*) of H_2CO were analyzed using this hybrid approach and were compared to recent quasiclassical trajectory calculations. The radical branching ratio was shown to increase rapidly with the total energy above the threshold for formation of those products, which is in qualitative, but not quantitative, agreement with the QCT results. The previous QCT radical branching ratio was found to decrease with *J* for a fixed total energy. This effect was captured in the present analysis and was traced to the positive shift in the threshold energy for the radical channel for fixed *E* as *J* increases. This shift was directly analyzed in terms of the centrifugal barriers on the potential and the direct consequences of angular momentum coupling. An analytical formulation of the energy threshold shifting due to centrifugal effects is derived and presented.

In this hybrid phase space formulation, one source of the discrepancy in the energy dependence of the combined phase space analysis is the neglect of the roaming pathway in the phase space analysis. The roaming pathway often is responsible for over 25% of the molecular products and therefore has a significant volume of phase space that should be included with the TS phase space. Another probable source of error is the assumption that all radical dissociation occurs through the MEP. Including multiple dissociation pathways that sample more of the PES could improve the PST analysis.

Straightforward phase space analysis was found to be in good agreement with the QCT rotational distribution of HCO and the dependence on *J*. The change in that distribution with increasing *J* was rationalized using PST. As the energy threshold moves to higher j_{HCO} with increasing *J*, the j_{HCO} distribution shifts toward higher values of *j*. PES anisotropy causes the minor disagreement between PST and QCT distributions at high j_{HCO} values, where the PST formulation assumes an isotropic PES replicating the MEP on all dissociation paths.

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