A classical trajectory study of the photodissociation of T_1 acetaldehyde: The transition from impulsive to statistical dynamics

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Previous experimental and theoretical studies of the radical dissociation channel of T_1 acetaldehyde show conflicting behavior in the HCO and CH_3 product distributions. To resolve these conflicts, a full-dimensional potential-energy surface for the dissociation of CH_3CHO into HCO and CH_3 fragments over the barrier on the T_1 surface is developed based on RO-CCSD(T)/cc-pVTZ(DZ) *ab initio* calculations. 20 000 classical trajectories are calculated on this surface at each of five initial excess energies, spanning the excitation energies used in previous experimental studies, and translational, vibrational, and rotational distributions of the radical products are determined. For excess energies near the dissociation threshold, both the HCO and CH_3 products are vibrationally cold; there is a small amount of HCO rotational excitation and little CH_3 rotational excitation, and the reaction energy is partitioned dominantly (>90% at threshold) into relative translational motion. Close to threshold the HCO and CH_3 rotational distributions are symmetrically shaped, resembling a Gaussian function, in agreement with observed experimental HCO rotational distributions. As the excess energy increases the calculated HCO and CH_3 rotational distributions are observed to change from a Gaussian shape at threshold to one more resembling a Boltzmann distribution, a behavior also seen by various experimental groups. Thus the distribution of energy in these rotational degrees of freedom is observed to change from nonstatistical to apparently statistical, as excess energy increases. As the energy above threshold increases all the internal and external degrees of freedom are observed to gain population at a similar rate, broadly consistent with equipartitioning of the available energy at the transition state. These observations generally support the practice of separating the reaction dynamics into two reservoirs: an impulsive reservoir, fed by the exit channel dynamics, and a statistical reservoir, supported by the random distribution of excess energy above the barrier. The HCO rotation, however, is favored by approximately a factor of 3 over the statistical prediction. Thus, at sufficiently high excess energies, although the HCO rotational distribution may be considered statistical, the partitioning of energy into HCO rotation is not. © 2006 American Institute of Physics. [DOI: 10.1063/1.2139672]

I. INTRODUCTION

Our understanding of reaction dynamics has developed from high-quality, highly resolved experimental and theoretical studies of the photodissociation dynamics of small molecules.^{1–8} Small systems allow highly accurate *ab initio* calculation of the electronic energy, which in turn can be used to generate a potential-energy surface (PES) for the reaction. A number of approaches have been used to generate PESs with the two most general being interpolation of the PES from *ab initio* data^{9–18} and the direct (“on the fly”) calculation of relevant electronic energies (and energy derivatives).^{19–21} A representation of the PES allows the dynamics of photodissociation to be simulated. The most accurate simulations employ quantum dynamics, although these calculations are very computationally intensive and have been employed, in full dimensionality, only for four-atom reactive systems.^{22,23}

As the molecule becomes larger and the degrees of freedom increase, the quality of both experimental data and the-

oretical modeling suffers. A high density of vibrational and rotational states makes experimental selection of initial state more difficult or impossible. Several electronic surfaces may play a role, and more than one chemical channel can be active even on a single electronic surface. For similar reasons, state-selective probing of product states is also problematic when the photoproducts are themselves polyatomic molecules; the number of product states increases rapidly, reducing the signal, and the spectroscopy becomes much more complex.

Over the past few years, experimentalists have made inroads into the measurement of highly resolved product state distributions for photodissociation of molecules of intermediate size, say, more than six atoms. In order to interpret their results, general theories or models, learned from the study of small molecules, are frequently used. These include an array of statistical theories, such as phase-space theory (PST),^{24,25} the statistical adiabatic channel model (SACM),^{26–28} and separate statistical ensembles (SSE).²⁹ These models, PST in particular, have been found to be appropriate in a number of cases where the reaction PES is a simple bound surface and the reaction dynamics are slow, allowing randomization of

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energy amongst the available degrees of freedom.^{30,31} Where the reaction takes place rapidly on a repulsive surface, there are an equivalent number of simple models, including the rotation-reflection principle (RRP)³² and the classical impulsive model,³³ along with many modifications.^{34,35} The intermediate case, where dissociation occurs over a barrier, is more problematic and one approach has been to divide the energy available to products into independent statistical and impulsive energy reservoirs.³⁶

Theoretical studies of reaction dynamics of larger molecules have advanced significantly over the past decade or so. *Ab initio* calculations of structure and energy can now be performed with chemical accuracy (a couple of kJ/mol) for moderately sized molecules,³⁷ although highly accurate calculations are still difficult, particularly for excited electronic states. The construction of a PES is also more difficult as the dimensionality of the system increases. Particular problems include the number of *ab initio* calculations required to accurately represent the PES, the rigorous treatment of molecular symmetry, the development of appropriate functional forms, and the treatment of redundant internal coordinates. Significant methodological advances, however, have allowed these problems to be addressed.^{14–18,38–40} Despite these advances, quantum-dynamical simulations are still prohibitive as the number of atoms (and the density of states) increases, and the simulation of reaction dynamics in larger molecules lies in the realm of classical or semiclassical mechanics.

One of the moderately sized polyatomic molecules that has been subjected to a large amount of experimental^{41–55} and theoretical^{43,48,56–63} scrutiny over the past decade is acetaldehyde. Acetaldehyde photodissociation serves as a simple model for the photodissociation of larger carbonyl compounds, many of which play a prominent role in air pollution and the formation of photochemical smog.

Acetaldehyde has two main dissociation channels, reactions (1a) and (1b) and a minor pathway when excited in the near ultraviolet, reaction (1c):⁵⁵

The radical products in channels (1a) and (1c) may also undergo subsequent dissociation to form $\text{CH}_3 + \text{CO} + \text{H}$. Figure 1 shows a schematic representation of the relevant electronic states in acetaldehyde photodissociation in the near ultraviolet. The photochemistry is initiated by excitation of acetaldehyde from the singlet ground state S_0 to S_1 via an $n-\pi^*$ transition in the ultraviolet region. The S_1 state may fluoresce or undergo internal conversion to highly excited vibrational states of S_0 or intersystem crossing to the T_1 state.^{44–46} The S_0 state correlates with both reactions (1a) and (1b). However, the barrier to production of $\text{CH}_4 + \text{CO}$ is significantly lower than for the C–C bond cleavage producing $\text{CH}_3 + \text{HCO}$,^{56,59} and therefore it is considered that only reaction (1b) is competitive on the S_0 surface. The T_1 surface correlates with production of CH_3 and HCO via a barrier in the exit channel. Experimentally, the HCO product has been

FIG. 1. Schematic diagram of the photodissociation of triplet acetaldehyde to CH_3 and HCO . $h\nu$ represents the excitation energy, E_{for} is the electronic energy barrier for the forward dissociation reaction, E_{rev} is the electronic energy barrier for the reverse, association reaction, E_{diss} is the electronic dissociation energy, E_{excess} is the excess energy at the transition state, and E_{avail} is the total available energy to the CH_3 and HCO products. The inset is the transition state structure for the photodissociation of triplet acetaldehyde, as calculated at UB3LYP/aug'-cc-pVTZ.

observed at photoexcitation wavelengths shorter than 320.5 nm ($31\,250\text{ cm}^{-1}$),^{41,44,46,51} which locates the top of the barrier at this energy. Huber suggests, on the basis of quantum beat experiments, a slightly higher threshold, between $31\,521$ and $31\,771\text{ cm}^{-1}$.⁶⁴ The S_0-T_1 origin transition has been observed experimentally at $27\,240\text{ cm}^{-1}$,⁶⁵ placing the barrier to radical dissociation on the triplet surface at 4010 cm^{-1} (48.0 kJ/mol). The barrier has also been estimated as between 4280 and 4530 cm^{-1} (51.2 to 54.2 kJ/mol), based on earlier experimental results.⁶⁴ The dissociation energy of S_0 acetaldehyde to $\text{CH}_3 + \text{HCO}$ has been estimated⁵⁰ to be $29\,225\text{ cm}^{-1}$ (349.6 kJ/mol) using standard thermochemical data⁶⁶ and the HCO heat of formation obtained by Chuang *et al.*⁶⁷ This value of the dissociation energy was recently used by Cruse and Softley to simulate the acetaldehyde radical fragment kinetic-energy profiles,⁴¹ and on this basis, Softley suggests an upper limit on the error in the dissociation energy of 300 cm^{-1} (3.6 kJ/mol).⁶⁸ We therefore estimate, using a threshold of $31\,250\text{ cm}^{-1}$, the barrier to radical association on the T_1 surface to be $2025 \pm 300\text{ cm}^{-1}$ ($24.2 \pm 3.6\text{ kJ/mol}$). This is comparable to an estimate of 23.8 kJ/mol by Kono *et al.*⁵⁰ The dissociation energy on the triplet surface can also be estimated at $(31\,250 \pm 300) - 29\,225 = 1985 \pm 300\text{ cm}^{-1}$ ($23.7 \pm 3.6\text{ kJ/mol}$).

The vibrationless equivalents of the energies discussed above are illustrated in Fig. 1. Considering only the triplet surface, we define the association barrier height or, equivalently, the reverse barrier height (E_{rev}) as the difference in electronic energy between the transition state and the products. We also define the dissociation energy (E_{diss}) as the

difference in electronic energy between the triplet equilibrium geometry and the products. The forward barrier height (E_{for}) is the sum of the reverse barrier height and the dissociation energy, corresponding to the difference in electronic energy between the equilibrium geometry and the transition state. There have been a number of *ab initio* investigations of the energetics of triplet state acetaldehyde and its dissociation to radicals.^{43,48,56,60,63} The best available *ab initio* estimates of the vibrationless electronic energy differences were calculated by King *et al.*,⁶⁰ using a focal-point extrapolation to approximate the CCSDT/CBS values, to be $E_{\text{rev}} = 1823 \text{ cm}^{-1}$ (21.8 kJ/mol), $E_{\text{for}} = 5545 \text{ cm}^{-1}$ (66.3 kJ/mol), and $E_{\text{diss}} = 3728 \text{ cm}^{-1}$ (44.6 kJ/mol). Adding in UB3LYP/TZ2Pf harmonic zero-point vibrational corrections yielded vibrationally corrected energies of 1583 cm^{-1} (18.9 kJ/mol) for the dissociation energy, 4732 cm^{-1} (56.6 kJ/mol) for the forward barrier, and 3149 cm^{-1} (37.7 kJ/mol) for the reverse barrier.

Several detailed experimental measurements have been made on the nature of the HCO product of reaction (1a). In those experiments, acetaldehyde in a free jet expansion was photolyzed and the HCO fragment probed using laser-induced fluorescence spectroscopy. The photolysis wavelengths varied between 280 and 320 nm,^{45–47,50} corresponding to energies ranging from threshold to about 25 kJ/mol above the barrier. Kono *et al.* estimated the rotational excitation by spectral fitting to be about 6.2 kJ/mol for initial energies from threshold to 25 kJ/mol above the barrier.⁵⁰ Terentis *et al.* measured the fully resolved rotational distribution, following excitation at 308 nm (15 kJ/mol above the barrier) which was again fitted to a Boltzmann distribution yielding an average of 7.1 kJ/mol rotational excitation.⁴⁷ They also reported no vibrational excitation in HCO and, via Doppler profiles, an average overall translational energy of 32 kJ/mol. Using energy and momentum balancing, they inferred little or no internal excitation of the methyl partner fragment.

The most definitive experiments on the HCO rotational distribution were carried out by Lee and Chen after they had performed a very detailed analysis of HCO spectroscopy.⁴⁶ They excited acetaldehyde at a range of energies from 0 to 25 kJ/mol above threshold. Their distributions were fitted to a Gaussian distribution, from which they obtained slightly lower values of rotational energy, ranging from 3.6 to 5.9 kJ/mol. They suggested that the extra energy might be partitioned into the methyl fragment.

Cruse and Softley have recently used velocity-map imaging to obtain images of both radical fragments following photodissociation of acetaldehyde at wavelengths 317.5–282.5 nm.⁴¹ These experiments indicate that the mean rotational energy of both the CH_3 and HCO fragments increases with photodissociation energy, with less rotational excitation in the CH_3 fragment, broadly consistent with an impulsive model for dissociation. They found that the lowest-frequency ν_2 umbrella mode in the CH_3 radical was excited for E_{avail} above 3000 cm^{-1} (35.9 kJ/mol). The observed CH_3 vibrational distribution was considerably colder than predicted us-

ing statistical models and indicated that the energy released on crossing the barrier was not partitioned into CH_3 vibrational excitation.

The classical dynamics of T_1 acetaldehyde dissociation have previously been studied by Cordeiro *et al.* using direct dynamics, where trajectories were initiated with 9.8 kJ/mol added to the zero-point vibrational energy at the transition state and the UB3LYP density functional was used with the 6–31G* basis set to determine the molecular energies and derivatives.⁵⁶ The excess energy at the transition state was chosen to correspond to the energy available following excitation at 308 nm and was partitioned into a microcanonical ensemble, from which 300 trajectories were propagated to a center-of-mass separation of 8 bohrs. The relative translational energy and rotational and vibrational product distributions were calculated. The predicted partitioning of the excess energy into rotational, vibrational, and translational modes indicated that the HCO fragment was vibrationally cold, losing energy relative to the initial zero-point energy during the trajectory simulation, but was rotationally excited, with an average rotational energy of 3.8 kJ/mol. The predicted HCO angular momentum distribution was found to peak at around $J=6$, in contrast to the experimental results, which peaked at around $J=10$ –14. The projection of the angular momentum distributions onto the HCO K_a axis revealed that only states with a low K_a were populated, and hence the rotational excitation about this axis was small. The CH_3 fragment, on the other hand, was found to be both vibrationally and rotationally excited, with an average vibrational energy of 10.5 kJ/mol above the zero-point vibrational energy and an average rotational energy of 2.9 kJ/mol. The relative translational energy of the products was predicted as 23.4 kJ/mol.

Direct dynamics calculations have also been carried out by Kurosaki and Yokoyama with 4.2 kJ/mol excess energy at the transition state using the UB3LYP/cc-pVDZ level of theory.⁵⁷ In this work 400 classical trajectories were calculated, zero-point energy was added to all nonimaginary frequency modes at the transition state, the excess energy of 4.2 kJ/mol was assigned to kinetic energy along the reaction coordinate, and the trajectories were terminated at 6 bohr separation. This study indicated that the vibrational energy of both products was approximately equal to their zero-point energy and hence vibrational excitation was negligible. The average CH_3 rotational energy was only 2.0 kJ/mol while the HCO rotational energy was significantly greater at 4.6 kJ/mol. The majority of the available excess energy was partitioned into translation, with the products having an average relative translational energy of 26.7 kJ/mol at dissociation.

In the preceding description, it is clear that there is a lack of consensus between the previous experimental and theoretical studies. The experimental distributions have been fitted to both Boltzmann distributions (implying statistical dynamics)^{47,50} and a Gaussian (implying impulsive dynamics).⁴⁶ One set of experiments suggests no change in HCO rotational excitation over the range from 0 to 25 kJ/mol above the barrier,⁵⁰ but another set shows an increase of 60% over the same range.⁴⁶ Previous *ab initio* stud-

ies have yielded a wide variety of critical energies, and the two previous trajectory studies disagree on the amount of internal excitation in the HCO and CH₃ fragments.^{56,57}

In this paper we determine a chemically accurate level of *ab initio* theory to investigate *T*₁ acetaldehyde radical dissociation. We then generate a reaction path for the radical dissociation and construct a full, multidimensional *ab initio* potential-energy surface as a second-order Taylor-series expansion about this reaction path, as implemented in our GROW computer program.^{14–18,38–40} We use this surface to calculate a statistically significant number of classical trajectories to determine the product vibrational and rotational energy distributions, for a range of initial excess energies spanning the excitation energies used in previous experimental studies. With the ensuing data we rationalize the experimental data, make a decision on the amount of internal excitation of the CH₃ fragment, and discuss the transition from impulsive to statistical behavior in the context of simple models of the photodissociation dynamics.

II. METHODS

A. Potential-energy surface construction

The potential-energy surface (PES) used in this work is given as an interpolation of Taylor polynomials centered at data points scattered throughout configuration space, according to the modified Shepard interpolation scheme developed by Collins and co-workers.^{14–18,38–40} This method has been described in detail previously, and we refer the reader to a recent review for further details³⁸ while summarizing the essential features of the scheme here. According to the modified Shepard interpolation scheme, the energy at an arbitrary molecular configuration is expressed as a weighted sum of Taylor polynomials about the N_d data points defining the PES data set and their symmetry equivalents:

$$V(\mathbf{Z}) = \sum_{g \in G} \sum_{i=1}^{N_d} w_{g \circ i}(\mathbf{Z}) T_{g \circ i}(\mathbf{Z}), \quad (2)$$

where $T_i(\mathbf{Z})$ is the Taylor-series expansion about the i th data point, truncated at second order:

$$\begin{aligned} T_i(\mathbf{Z}) = & V[\mathbf{Z}(i)] + \sum_{k=1}^{3N-6} [Z_k - Z_k(i)] \left. \frac{\partial V}{\partial Z_k} \right|_{\mathbf{Z}=\mathbf{Z}(i)} \\ & + \frac{1}{2!} \sum_{k=1}^{3N-6} \sum_{j=1}^{3N-6} [Z_k - Z_k(i)] \times [Z_j - Z_j(i)] \\ & \times \left. \frac{\partial^2 V}{\partial Z_k \partial Z_j} \right|_{\mathbf{Z}=\mathbf{Z}(i)}, \end{aligned} \quad (3)$$

and w_i is the normalized weight function, which gives the contribution of the i th Taylor expansion to the potential energy at configuration $\mathbf{Z}$. w_i is given by the equations:

$$w_i(\mathbf{Z}) = \frac{v_i(\mathbf{Z})}{\sum_{g \in G} \sum_{i=1}^{N_d} v_{g \circ i}(\mathbf{Z})}, \quad (4)$$

$$v_i(\mathbf{Z}) = \left\{ \left[\sum_{k=1}^{N(N-1)/2} \left(\frac{\|\mathbf{Z} - \mathbf{Z}_k\|}{d_k(i)} \right)^2 \right]^q + \left[\sum_{k=1}^{N(N-1)/2} \left(\frac{\|\mathbf{Z} - \mathbf{Z}_k\|}{d_k(i)} \right)^2 \right]^p \right\}^{-1}, \quad (5)$$

where $v_i(\mathbf{Z})$ is the un-normalized two-part weight function, which includes $d_k(i)$ terms, which are confidence lengths derived from Bayesian analysis of the interpolation data.⁴⁰ For all simulations carried out in this paper, the weight powers q and p were 2 and 15, respectively, and the confidence lengths were determined by the distances of the ten closest data points within an energy tolerance of 0.5 kJ/mol.

The notation $g \in G$ denotes the inclusion of all g elements from the permutation group G , which acts to interchange symmetry-equivalent atoms. Accordingly, the notation $g \circ i$ denotes that the i th data point is transformed by the group element g . The coordinate system $\mathbf{Z}$, in which the PES is constructed, is the inverse interatomic distances $\mathbf{Z} = \{1/R_1, 1/R_2, \dots, 1/R_{3N-6}\}$. For this system, the permutation group G is sym(3), the symmetric group of all permutations of the three hydrogens. In this manner, the interpolated PES is guaranteed to possess the correct nuclear permutation and inversion symmetry.

The quality of the PES produced depends on two factors: the *ab initio* theory used to generate the derivative data for the Taylor polynomials and the location of the PES data points in configuration space.

In order to determine the level of *ab initio* theory to use in constructing the PES, benchmarking was carried out by calculating the energies of geometries along the minimum-energy path (MEP) using UB3LYP (Refs. 69 and 70) and RO-CCSD(T) (Refs. 71 and 72) with both double-zeta and triple-zeta Pople^{73–78} and Dunning basis sets.^{79–92} For comparative purposes we used a MEP generated by performing UB3LYP/aug'-cc-pVTZ geometry optimizations for a series of constrained C–C distances starting from 1.38 Å, corresponding to the optimized triplet acetaldehyde geometry, and increasing in 0.1 Å steps. The energy profiles along this path were examined as a function of basis-set size and *ab initio* method. As described in Sec. III A, we chose to construct the triplet PES using the restricted open-shell coupled-cluster method with single and double excitations and with noniterative inclusion of triple excitations [RO-CCSD(T)].^{71,72} The basis set used was a composite basis set, consisting of the Huzinaga-Dunning correlation-consistent valence triple-split basis set^{79–82} (cc-pVTZ) on the carbon atoms, the Huzinaga-Dunning correlation-consistent valence double-split basis set^{79,80} (cc-pVDZ) on the oxygen atom, and the Dunning double-zeta⁸⁰ (DZ) basis set on the hydrogen atoms. We have denoted this method as RO-CCSD(T)/cc-pV(TZ/DZ). We consider that this combination of method and basis set represents the best current compromise between accuracy and computational feasibility. First derivatives of the energy with respect to atomic displacement were calculated analytically and second derivatives were calculated by numerical differencing of first derivatives, as implemented in the ACES II *ab initio* electronic structure code.⁸³

FIG. 2. Approximations to the minimum-energy path profiles for the dissociation of T_1 acetaldehyde, using UB3LYP/cc-pVTZ optimized geometries.

Given the computational cost of obtaining accurate data, we could not afford to implement the full GROW algorithm.^{14–18,38–40} Rather than updating the data set with new *ab initio* data after running some number of trajectories, we simply present here the results of classical trajectories calculated on the final global PES which was interpolated from RO-CCSD(T)/cc-pVTZ(DZ) calculations along a 16-point MEP optimized at UB3LYP/aug'-cc-pVTZ, with the transition state geometry fully optimized at RO-CCSD(T)/cc-pVTZ(DZ). A further data point was added at a C-C distance of 3.58 Å to provide adequate long-range data to model the dissociated products. The 17 data points describing the MEP are illustrated, in terms of C-C bond length, in Figs. 2(a) and 2(b).

All UB3LYP calculations were carried out using the GAUSSIAN 03 suite of quantum-chemical programs⁸⁴ and all RO-CCSD(T) calculations were carried out using the ACES II suite of quantum-chemical programs⁸³ on computer facilities at the Australian Partnership for Advanced Computing (APAC) National Facility.

B. Trajectory simulations

The classical trajectories were initiated at the transition state for the photodissociation of acetaldehyde by fixing the C-C distance to 1.98 Å and sampling the initial coordinates and momenta for the other degrees of freedom from a microcanonical distribution^{85,86} for fixed vibrational energies of 2.52, 6.82, 11.53, 18.26, and 24.38 kJ/mol, corresponding to the excitation energies reported by Lee and Chen.⁴⁶ The

zero-point vibrational energy was not taken into account when determining these quantities as it is unclear how to properly account for quantum zero-point motion within a classical trajectory simulation. The nonphysical leakage of zero-point energy during a classical trajectory simulation is known to affect the calculated dynamical properties^{87–92} and is likely to be particularly important for high-energy vibrational modes (such as the C-H stretches in the CH₃ moiety). Although there have been a number of methods proposed to conserve zero-point energy in classical trajectories,⁹³ we have taken the simple expedient of neglecting it in these calculations. Trajectories were initiated with zero angular momentum, consistent with experiment: the rotational degrees of freedom of the acetaldehyde parent molecule are efficiently cooled in a supersonic expansion. For each set of initial conditions considered, four sets of 5000 trajectories were run for 24 fs or until the molecule had dissociated, as indicated by the product fragments reaching a 5.3 Å (11 bohrs) separation. The angular momentum, internal vibrational energy, and relative translational energy product distributions were then obtained by binning the final values of each of these quantities for the reactive trajectories.

III. RESULTS

A. Energetics and PES construction/PES topology

The results of the classical dynamics simulations are determined by the topology of the exit channel and it is therefore necessary to construct the PES from *ab initio* data that faithfully reproduces the known features of this region of the surface. The most obvious reference point is the experimentally determined association barrier for the CH₃+CHO → CH₃CHO reaction; the difference in energy between the transition state and the separated products. However, the experimentally determined energies implicitly include zero-point vibrational energy, which can only be approximately modeled by including a harmonic zero-point correction to the energy at each static configuration. The heat of formation data used experimentally to determine the energy of the separated radical product fragments may also be a source of error. Therefore, high-level *ab initio* calculations also provide a useful reference point in benchmarking more approximate *ab initio* methods.

The relative energies of the stationary points along the photodissociation reaction path, as determined experimentally and theoretically, are presented in Table I, and the transition state structure, calculated at UB3LYP/aug'-cc-pVTZ, is illustrated in the inset of Fig. 1. From Table I, we observe that UB3LYP consistently underestimates the reverse barrier height with respect to the complete basis-set limit, focal-point calculations of King *et al.*⁶⁰ by up to 10.6 kJ/mol. Figure 2 presents approximations to the minimum-energy profile (MEP) for radical dissociation on the T_1 surface. The points illustrated in Fig. 2(a) were obtained by performing single point energy calculations at various levels of theory at geometries generated along the optimized UB3LYP/aug'-cc-pVTZ MEP. Inspection of Fig. 2(a) reveals that the UB3LYP MEP is quantitatively different from MEPs calculated using high-level *ab initio* theory. This is in agreement

TABLE I. Vibrationless relative energies (kJ/mol) with respect to the equilibrium structure, for the forward and reverse energy barriers, E_{for} and E_{rev} , respectively, and the dissociation energy E_{diss} for the photodissociation of triplet acetaldehyde. See text and Fig. 1 for definition of energetics.

Method	E_{for}	E_{rev}	E_{diss}	Reference
CISD+SCC/3-21G//HF/3-21G	88.6	28.0	60.6	63
UCCSD(T)/cc-pVDZ	69.9	26.7	43.2	60
UCCSD(T)/cc-pVTZ	68.1	25.1	43.0	60
Extrapolated UCCSDT/CBS	66.4	21.8	44.6	60
UB3LYP/cc-pVDZ	71.5	12.1	59.4	57
UMP2/cc-pVDZ	71.5	56.0	15.5	57
UB3LYP/6-31+G*	72.0	11.2	60.8	This work
UB3LYP/6-311G**	63.9	16.5	47.4	This work
UB3LYP/cc-pVDZ	69.2	14.1	55.1	This work
UB3LYP/cc-pVTZ	62.8	16.6	46.2	This work
RO-CCSD(T)/6-31+G*	78.9	34.9	44.0	This work
RO-CCSD(T)/6-311G**	70.3	36.1	34.2	This work
RO-CCSD(T)/cc-pVDZ	70.8	37.0	33.8	This work
RO-CCSD(T)/cc-pV(TZ/DZ)	73.9	28.1	45.7	This work
Experiment ^a	48-54	24.2±3.6	23.7±3.6	See text

^aImplicitly includes zero-point energy corrections.

with previous studies, which have found that UB3LYP predicts a transition state at a C–C distance of 0.1 Å longer than that predicted using CCSD(T).⁵⁶ We therefore conclude that UB3LYP does not accurately describe the exit channel and a more accurate method must be used to describe the PES in this region. From Table I, we observe that RO-CCSD(T) overestimates the reverse barrier height, by up to 15.2 kJ/mol. However, increasing the size of the basis set on the carbon atoms results in both a significant decrease in the predicted association barrier height and a qualitative change in the MEP profile, as illustrated in Fig. 2(b). Figure 2(b) was generated, similarly to Fig. 2(a), by performing RO-CCSD(T) single point energy calculations using various basis sets, at geometries along the optimized UB3LYP/aug'-cc-pVTZ MEP. The variation with basis set observed in Fig. 2(b) is consistent with the physics of the reaction: The largest geometrical change occurs around the two carbon atoms involved in the bond-breaking process. A larger basis set provides the flexibility necessary to more accurately describe this change. Increasing the number of basis functions on the hydrogen atoms, however, has little effect on the relative energies or MEP profile. Therefore, the small DZ basis set was used to describe the hydrogen atoms and reduce the computational expense of the calculations. The final PES was obtained by a reaction path expansion, using RO-CCSD(T)/cc-pVTZ(DZ) energies, gradients, and second derivatives, calculated along the optimized UB3LYP/aug'-cc-pVTZ MEP, but using a data point corresponding to the fully optimized RO-CCSD(T)/cc-pVTZ(DZ) transition state. Although increasing the basis set on the carbon atoms to a correlation-consistent triple-zeta basis significantly increased the quality of the PES, our calculations still fall short of the UCCSDT/CBS results of King *et al.*,⁶⁰ overestimating the reverse barrier height by 6.3 kJ/mol. It is not currently feasible for us to calculate even a 17-point MEP expansion of the PES at the UCCSDT/CBS level of theory. Our RO-CCSD(T)/cc-pVTZ(DZ) calculations, however, pro-

vided a similar imaginary frequency at the transition state, 484i cm⁻¹, to that calculated by King *et al.*, 516i cm⁻¹,⁶⁰ which are in contrast to the value of 60i cm⁻¹ obtained from Rice-Ramsperger-Kassel-Marcus (RRKM) fits to the experimental data.⁴³ Including RO-CCSD(T)/cc-pVTZ(DZ) harmonic zero-point energy corrections at the stationary point geometries yielded a corrected association barrier height of 39.1 kJ/mol which compares with a best theoretical estimate of 37.7 kJ/mol.⁶⁰ In terms of assessing the product distributions from the reaction, it is important to note that we have estimated the experimental association barrier height at 24±4 kJ/mol and, because our trajectory calculations do not include zero-point energy, our simulations therefore overestimate the available energy at the product configuration by approximately 4 kJ/mol.

B. Dynamics

The vibrational and rotational product distributions of the HCO and CH₃ fragments, determined from the classical trajectory simulations, are presented in Figs. 3 and 4. The relative translational energy distribution is illustrated in Fig. 5. In each of these figures the distributions corresponding to the lowest (2.5 kJ/mol) and highest (24.4 kJ/mol) excess energy are illustrated with a heavy line, while curves corresponding to intermediate E_{excess} have light weight lines. The average energies partitioned to the various product degrees of freedom are summarized in Table II as a function of excess energy at the transition state, E_{excess} . These were calculated as the average over all reactive trajectories for the given value of E_{excess} . The number of reactive trajectories analyzed, from the total of 20 000 calculated, ranged from 17 580 at $E_{\text{excess}}=2.5$ kJ/mol to 14 403 at $E_{\text{excess}}=24.4$ kJ/mol. Errors have not been included in Table II; however, twice the standard error of the mean ranges from approximately 0.01 kJ/mol at $E_{\text{excess}}=2.5$ kJ/mol to approximately 0.10 kJ/mol at $E_{\text{excess}}=24.4$ kJ/mol. Despite the fact that

FIG. 3. Vibrational energy distributions for HCO and CH_3 calculated for five different excess energies (labeled in kJ/mol). The data and labels for the highest and lowest excess energies are shown in bold. The energy of the lowest vibrational levels in HCO and CH_3 , the HCO bend at 1081 cm^{-1} (12.9 kJ/mol) (Ref. 94), and umbrella mode (606 cm^{-1} or 7.25 kJ/mol) (Ref. 95), respectively, are indicated by arrows.

these errors are small, by virtue of the large number of calculated trajectories, the values in Table II have been quoted only to a single decimal place in recognition of the approximate nature of the underlying potential-energy surface. In particular, our non-zero-point-corrected RO-CCSD(T)/cc-pVTZ(DZ) reverse barrier height was found to be 28 kJ/mol , compared to an experimental, zero-point-corrected value of approximately 24 kJ/mol .

The product distributions are discussed separately below.

1. Vibrational distributions

The HCO product vibrational distributions are shown in Fig. 3. Near threshold, at $E_{\text{excess}} = 2.5\text{ kJ/mol}$, we predict an overall partitioning of 1.2 kJ/mol into the vibrational degrees of freedom of the HCO fragment, which constitutes 4% of the available energy. We also found that 99% of the reacting trajectories generated at $E_{\text{excess}} = 2.5\text{ kJ/mol}$ resulted in an HCO vibrational energy $E_{\text{vib}} < 2.75\text{ kJ/mol}$. For comparison the lowest-energy vibrational state of HCO is the bend with a frequency of 1081 cm^{-1} (12.9 kJ/mol).⁹⁴ The trajectory calculations therefore suggest that, for dissociation of acetaldehyde at threshold, the HCO fragments are born vibrationally cold, with population solely in the ground $v=0$ state.

At larger E_{excess} the vibrational energy of HCO increases, both in absolute and relative terms (see Table II). At the

FIG. 4. Rotational energy distributions for HCO and CH_3 calculated for the labeled five different excess energies. The distributions for the highest and lowest E_{excess} are shown in bold. The distributions change from symmetric “Gaussian shaped” at low energy to more asymmetric “Boltzmann shaped” at higher energy.

highest E_{excess} surveyed here, 24.4 kJ/mol , the HCO vibrational energy has risen to an average of 4.8 kJ/mol , 9% of E_{avail} . In this case 99% of all reacting trajectories had $E_{\text{vib}} < 13.5\text{ kJ/mol}$. Again, for most trajectories, the vibrational

FIG. 5. Total translational energy distributions calculated for five different excess energies (labeled in kJ/mol). The data and labels for the highest and lowest excess energies are shown in bold. The energy of the exit channel (E_{rev}) is shown as an arrow and indicates that most of the exit channel energy is partitioned into translational energy.

TABLE II. Energy partitioning (kJ/mol) amongst rotational, E_{rot} , vibrational, E_{vib} , and relative translational, E_{trans} , degrees of freedom for $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{HCO}$ photoproducts initiated with E_{excess} energy (kJ/mol) at the transition state and with E_{avail} (kJ/mol) energy at the product configuration.

E_{excess}	E_{avail}	E_{vib}		E_{rot}		E_{trans}	Reference
		CH_3	HCO	CH_3	HCO		
Classical trajectories							
4.2	30.5	−0.8	−2.1	2.0	4.6	26.7	57 ^a
9.8	32.4	10.5	−8.2 ^b	2.9	3.8	23.4	56 ^a
2.5	30.6	1.4	1.2	0.6	1.2	26.2	This work
6.8	34.9	2.5	1.8	0.9	2.0	27.7	This work
11.5	39.7	4.0	2.7	1.4	3.3	28.3	This work
18.3	46.4	6.1	3.8	2.0	4.8	29.7	This work
24.4	52.5	8.6	4.8	2.9	6.3	29.8	This work
Impulsive reservoir							
0	28.1	0.4	0.7	0.2	0.5	26.3	
Impulsive reservoir plus equipartition of energy at the transition state							
24.4	52.5	10.8	6.0	2.9	3.1	29.8	

^aEnergies are with respect to harmonic zero-point energy at transition state and product configurations. This gives a ZPE-corrected reverse barrier height of 26.4 and 22.6 kJ/mol for Refs. 57 and 56, respectively.

^bThis value was not given in Ref. 56; although the HCO fragment was stated to lose energy with respect to its harmonic zero-point energy, it was determined here via conservation of energy.

energy is small relative to the lowest excited vibrational state of HCO. At $E_{\text{excess}}=24.4$ kJ/mol we would predict a small $\nu=1$ population in the bending vibration but with HCO formed predominantly in the $\nu=0$ ground state.

The CH_3 vibrational distributions as a function of E_{excess} are also illustrated in Fig. 3 and are hotter than for HCO. Near threshold, at $E_{\text{excess}}=2.5$ kJ/mol, the CH_3 vibrational energy distribution is narrow with an average of 1.4 kJ/mol and with 99% of trajectories having $E_{\text{vib}}(\text{CH}_3) < 3.0$ kJ/mol, insufficient to excite even the lowest-frequency methyl vibration, the ν_2 methyl umbrella motion at 606 cm^{-1} (7.2 kJ/mol).⁹⁵ As E_{excess} rises, however, the partitioning of available energy into CH_3 vibration rises rapidly. At $E_{\text{excess}}=24.4$ kJ/mol, the average CH_3 vibrational energy is 8.6 kJ/mol, comprising 16% of the available energy and sufficient to excite the methyl umbrella mode. Indeed, for these initial conditions, we would expect more population in $\nu=1$ of the umbrella mode than in $\nu=0$.

2. Rotational distributions

The final HCO rotational energy distributions, as shown in Fig. 4, were binned according to the total angular momentum J and then normalized. The trajectory simulations initiated near threshold display a relatively narrow, symmetric (“Gaussian-shaped”) angular momentum distribution. As E_{excess} increases, the angular momentum distribution broadens asymmetrically until, for the highest excess energies considered, the distribution more closely resembles a Boltzmann-type distribution (*vide infra*). At $E_{\text{excess}}=2.5$ kJ/mol the average HCO rotational energy at threshold is 1.2 kJ/mol (4% of E_{avail}). This fraction climbs steeply with excess energy, reaching 6.3 kJ/mol (12% of E_{avail}) at $E_{\text{excess}}=24.4$ kJ/mol.

The CH_3 fragment angular momentum distributions, also shown in Fig. 4, are similar in shape to the HCO distribu-

tions, changing from a symmetric Gaussian shape to a more asymmetric Boltzmann distribution with increasing excitation energies. The CH_3 rotational product distributions, however, are narrower and shifted to lower angular momentum than their HCO counterparts. We obtain an average rotational energy of 0.6 kJ/mol (Table II) for trajectories initiated with $E_{\text{excess}}=2.5$ kJ/mol, rising only to 2.9 kJ/mol for $E_{\text{excess}}=24.4$ kJ/mol. This degree of freedom is the most difficult to excite across the range of excess energies studied here.

3. Translational energy distributions

The average relative translational energies of the HCO and CH_3 photoproducts were found to vary between 26.2 and 29.8 kJ/mol, depending on the initial excess energy of acetaldehyde at the transition state, as illustrated in Fig. 5 and shown in Table II. This increase as a function of E_{excess} is quite modest and the proportion of the available energy partitioned into relative translation falls from 86% to 57% as E_{excess} increases from 2.5 to 24.4 kJ/mol. Despite the modest increase in translational energy, Fig. 5 shows the distribution to broaden significantly as excess energy is added to the reaction.

IV. DISCUSSION

Overall, our trajectory results reveal a picture of acetaldehyde photodissociation dynamics that shifts from the one dominated by translational energy release near threshold (at $E_{\text{excess}}=2.5$ kJ/mol 86% of all available energy is released as translational energy) towards a more equitable distribution of available energy amongst the internal and external degrees of freedom as energy is increased above the barrier. In the following sections we compare our results with previous experimental and theoretical results, which are included in Tables II and III. Finally, we examine the changes in product

TABLE III. Experimental energy partitioning (kJ/mol) amongst rotational, vibrational, and relative translational degrees of freedom for $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{HCO}$ photoproducts. The values of E_{avail} (kJ/mol) are as reported in the original work, while E_{excess} (kJ/mol) assumes a 24 kJ/mol exit channel barrier.

Energetics ^a		E_{vib}		E_{rot}		E_{trans}	Reference and comment
E_{excess}	E_{avail}	CH_3	HCO	CH_3	HCO		
<14.1	<38.1		0		6.2		Refs. 49 and 51. Threshold for HCO vibrational excitation at $E_{\text{excess}} = 14.1$ kJ/mol. Rotational energy calculated using Boltzmann distribution.
>14.1	>38.1		>0		6.2		
15	39	(0) ^b	0	(0) ^b	7.1	32	Ref. 47. Rotational and translational energies calculated assuming Boltzmann distribution.
3.5	27.5		0		3.6		Ref. 46. Best measurements of HCO rotational energy. Average rotational energy calculated from direct averaging.
7.8	31.8		0		3.9		
12.5	36.5		0		4.5		
19.3	43.3		0		4.9		
25.4	49.4		0		5.9		
4.8	28.8	0		1.2			Ref. 41. Best translational measurements. Average rotational energy calculated assuming Boltzmann distribution.
9.1	33.1	0		1.5	3.7		
11.9	35.9	>0 ^c					
18.2	42.2	>0	(0) ^b	2.5	6.2	33.4	
20.0	44.0	>0			6.9		

^aSee text and Fig. 1 for definition of energetics.

^bInferred rather than measured.

^c $E_{\text{excess}} = 11.9$ kJ/mol was established as the threshold for CH_3 vibrational excitation.

distributions with increasing energy and make connections with some of the simpler models of energy partitioning that are favored by experimentalists.

A. Comparison with experiments

There have been a number of experimental measurements of the photodissociation dynamics of acetaldehyde in the past decade or so.^{41,46,47,49,51} Most of these have been in the energy range studied here (i.e., 0–25 kJ/mol above the triplet barrier) and many of the relevant data are summarized chronologically in Table III. Although some of the older data have become redundant as better measurements have arisen, the results of all four experimental groups hold together to present a consistent picture of the dynamics of acetaldehyde dissociation over this energy range. Furthermore all four experimental groups used consistent thermochemical values, which make it easier to compare them. A thermochemical bond dissociation energy (i.e., ground state of acetaldehyde to ground state of products) of 348 ± 1 kJ/mol (29100 ± 100 cm⁻¹) was used in each case. The threshold for $\text{HCO} + \text{CH}_3$ production was measured or assumed to be 372 kJ/mol ($31\,100$ cm⁻¹) in all cases except Lee and Chen,⁴⁶ who reported a value 300 cm⁻¹ higher, although they also reported product state distributions for lower excitation energies than this. In Table III, we have used the values of E_{avail} from the original papers (which are all consistent), but we have used a value of 24 kJ/mol for E_{rev} in order to calculate E_{excess} . The values of E_{excess} given in Table III are the same as those in the original papers with the exception of Lee and Chen,⁴⁶ which are slightly higher in Table III than were quoted in their original work.

In comparing experiment with the theoretical energy distributions in this work, we must be mindful that the exit

channel height E_{rev} arising from our potential surface is 28 kJ/mol. This value for E_{rev} was used by Lee and Chen,⁴⁶ however, we feel a more reliable experimental estimate to be 24 ± 4 kJ/mol. We have also chosen to use E_{excess} rather than E_{avail} to compare with experiment because we want to specifically examine how excess energy above the barrier is distributed into the various internal and external degrees of freedom of the product fragments.

In comparing our predicted energy distributions with those from experiment, there are two aspects that we consider semi-independently: the *absolute value* of the average energy and distributions and the *shape* of the distributions, in particular, the way in which shape changes with E_{excess} .

1. Vibrational distributions

All four experimental groups measured the vibrational energy of the HCO fragment, either directly using laser-induced fluorescence (LIF) spectroscopy^{46,47,49,51} or indirectly from the recoil of the sibling methyl fragment.⁴¹ There is complete agreement that HCO is born only in the $v=0$ state for low excess energy. Gejo *et al.*⁴⁹ measured the appearance threshold for the (0,0,1) bending vibration to be approximately 1200 cm⁻¹ above the barrier ($E_{\text{excess}} = 14.1$ kJ/mol), but with no significant population until $E_{\text{excess}} \approx 39$ kJ/mol, where the population in (0,0,1) was about 10% of that in the (0,0,0) level.

Our data in Fig. 3 likewise show that the classical vibrational energy in HCO remains below that required for excitation of any vibrational mode at all excess energies studied here.

The experiments of Terentis *et al.* inferred, for $E_{\text{excess}} = 15$ kJ/mol, little or no vibrational excitation of the CH_3 fragment,⁴⁷ although Lee and Chen suggest, for E_{excess} be-

tween 0 and 25 kJ/mol, that some energy may be partitioned into the CH₃ vibrations.⁴⁶ Cruse and Softley inferred the CH₃ vibrational energy from the appearance of distinct peaks in the HCO translational distribution, which they attributed to vibrationally excited methyl.⁴¹ They found no CH₃ vibrational excitation for $E_{\text{avail}} < 3000 \text{ cm}^{-1}$ ($E_{\text{excess}} = 11.9 \text{ kJ/mol}$), but above this available energy a peak in the translational energy distribution is observed which they attributed to excitation of the ν_2 methyl umbrella mode. They found that the population in ν_2 increased strongly with E_{excess} and saw, for $E_{\text{excess}} = 43.3 \text{ kJ/mol}$, four distinct peaks in the HCO kinetic-energy distribution. The first two of these corresponded to ground-state CH₃ and excitation of the ν_2 umbrella mode. The assignments of the other two bands were inconclusive.

Our trajectory results are consistent with the experimental results of Terentis *et al.*⁴⁷ and Cruse and Softley.⁴¹ At $E_{\text{excess}} = 11.5$ and 18.3 kJ/mol the vibrational excitation of CH₃ is small. As E_{excess} increases to 24.4 kJ/mol, however, we expect the population of CH₃ with one quantum excitation in the ν_2 umbrella mode to increase strongly, as shown in Fig. 3 and Table II.

2. Rotational distributions

The HCO nascent rotational distribution in this system has been the most extensively explored experimentally, having been measured at a variety of excess energies above the barrier by all four groups. The earliest experiments inferred a Boltzmann distribution with $E_{\text{rot}} = 6.2 \text{ kJ/mol}$ that was invariant to E_{excess} over the range studied here.^{49,51} Terentis *et al.* also fitted a Boltzmann distribution with $E_{\text{rot}} = 7.1 \text{ kJ/mol}$ at 15.3 kJ/mol excess energy.⁴⁷ Lee and Chen carried out the most extensive characterization of the HCO rotational distribution.⁴⁶ They measured a non-Boltzmann population distribution, which led to lower average values of E_{rot} , ranging from 3.6 kJ/mol for dissociation near threshold to 5.9 kJ/mol for $E_{\text{excess}} = 24.4 \text{ kJ/mol}$. In their velocity map imaging experiments, Cruse and Softley assumed a Boltzmann distribution of HCO rotational states and inferred the HCO rotational energy to rise from 3.7 to 6.9 kJ/mol, for values of E_{excess} from 9.1 and 20.0 kJ/mol (E_{avail} between 33.1 and 44.0 kJ/mol).⁴¹ In general, experiments that used a Boltzmann population distribution resulted in higher average values of HCO rotational energy. Lee and Chen, who fitted a Gaussian function to their data, inferred lower average values of E_{rot} for HCO because a Gaussian function does not have a high-energy tail.

The qualitative trends in our trajectory data are of worth closer examination. Firstly, as shown in Table II, the average rotational energy in HCO increases linearly with E_{excess} —a trend observed by both Lee and Chen⁴⁶ and Cruse and Softley.⁴¹ Secondly, the shapes of the HCO rotational distributions in Fig. 4 bear closer scrutiny. The product state distribution at the lowest available energy is quite symmetric and resembles a Gaussian curve as suggested by Lee and Chen.⁴⁶ As the energy is raised the population spreads asymmetrically to higher J . This gives the distribution a shape that is less Gaussian and resembles more a Boltzmann distribution as inferred by Terentis *et al.*⁴⁷ and Cruse and Softley.⁴¹

The difference in interpretation between a Gaussian and Boltzmann curve is considered further later in the Discussion.

Our predicted HCO rotational distributions are generally narrower and shifted to lower energies than the experimentally determined distributions. The calculated trajectories and the resultant product distributions are highly sensitive to the topology of the PES and the difference between the experimental and theoretical distributions may simply be due to the incompleteness of our PES. The PES was mapped out in detail only along the C–C bond-stretching coordinate, and all other coordinates were accounted for by a second-order Taylor-series expansion in inverse bond-length coordinates about the data points along this minimum-energy path. That is, we did not include geometries that would specifically describe rotational motion of the products.

Another possible cause of error in our calculated product distributions is quantum zero-point motion. Our simulations attribute up to 5 kJ/mol of vibrational energy to the HCO fragment, which, as discussed above, is significantly below the first quantized vibrational state. To better model the experiment, this classical vibrational energy would need to be redistributed to the other degrees of freedom, which would potentially increase the HCO rotational energy.

Terentis *et al.* suggested that the amount of CH₃ rotational energy should be small, based on both conservation of energy in their experimental data and arguments based on the structure of the transition state: The impulsive force in C–C bond fission is exerted close to the methyl center-of-mass making it difficult to excite CH₃ rotation.⁴⁷ The only measurement of methyl rotational energy comes from the experiments of Cruse and Softley.⁴¹ They assumed a Boltzmann population distribution of CH₃ rotational states to simulate the HCO kinetic-energy distribution and considered only E_{excess} from 4.5 to 18.2 kJ/mol (E_{avail} from 28.8 to 42.2 kJ/mol) to avoid vibrational excitation of the CH₃ fragment. They obtained average CH₃ rotational energies increasing from 1.2 kJ/mol ($E_{\text{excess}} = 4.5 \text{ kJ/mol}$) to 2.5 kJ/mol ($E_{\text{excess}} = 18.2 \text{ kJ/mol}$). The good fit they obtained for the HCO kinetic-energy distribution suggests that the assumption of a Boltzmann population distribution is reasonable under their experimental conditions.

Our trajectory results are in good accord with both observations. The CH₃ rotational energy is indeed modest; it is the reservoir that is most difficult to deposit energy into for exactly the reasons used by Terentis *et al.*⁴⁷ Near threshold, at $E_{\text{excess}} = 2.5 \text{ kJ/mol}$, $E_{\text{rot}}(\text{CH}_3)$ is only 0.6 kJ/mol. The average CH₃ rotational energy increases with E_{excess} because of added vibrational motion in the acetaldehyde parent at the transition state. The absolute magnitude of our values of E_{rot} and the rate of its increase with E_{excess} are in good agreement with the experiments although we predict E_{rot} generally slightly lower than experiment, as was observed for HCO rotation.

3. Translational distributions

The first experimental estimate of the relative translational energies was obtained by Terentis *et al.*⁴⁷ who obtained an upper estimate of the HCO translational energy of

11 kJ/mol ($E_{\text{excess}} = 15$ kJ/mol) by analysis of the Doppler linewidths of low-energy peaks in the HCO LIF spectrum. Conservation of linear momentum allowed the translational energy of CH_3 to be inferred as 21 kJ/mol, and hence a value of 32 kJ/mol was obtained for the product translational energy.

Cruse and Softley measured the recoil kinetic-energy distribution directly using velocity map imaging of each fragment independently.⁴¹ They did not, however, report average translational energies. Their paper shows the kinetic-energy distribution for each fragment at $E_{\text{excess}} = 18.2$ kJ/mol, and from the analysis of their published data we obtain $E_{\text{trans}}(\text{HCO}) = 12.1$ kJ/mol and $E_{\text{trans}}(\text{CH}_3) = 21.4$ kJ/mol. The sum provides a total product translational energy of 33.4 kJ/mol, in agreement with the earlier, less precise measurements.

The translational energies obtained from our trajectory calculations are in agreement with the experiments. Indeed, it is this degree of freedom that was mapped in the global PES and so we expect this distribution from trajectory calculations to be the most reliable. Our values of E_{trans} increase from 26.2 kJ/mol at $E_{\text{excess}} = 2.5$ kJ/mol to 29.8 kJ/mol for $E_{\text{excess}} = 24.4$ kJ/mol. At $E_{\text{excess}} = 18.3$ kJ/mol our value of 29.7 kJ/mol agrees well with Cruse and Softley's results. These values are slightly lower than the experimental results but again we expect that the redistribution of the classical vibrational energy of the fragments would increase them slightly.

B. Comparison with previous theoretical studies

There have been two previous classical trajectory studies of the photodissociation of T_1 acetaldehyde. Cordeiro *et al.* calculated 300 trajectories at $E_{\text{excess}} = 9.8$ kJ/mol (Ref. 56) and Kurosaki and Yokoyama calculated 400 trajectories with $E_{\text{excess}} = 4.2$ kJ/mol.⁵⁷ Both studies employed direct dynamics with the electronic energies and gradients calculated using the UB3LYP density functional. Both also included zero-point energy at the transition state with Cordeiro *et al.* using microcanonical sampling to partition the initial excess energy whereas Kurosaki and Yokoyama assigned it to the reaction coordinate. The results of these studies are summarized in Table II.

1. Vibrational distributions

Our trajectory calculations suggest that, for dissociation of acetaldehyde near threshold, the HCO fragment is born vibrationally cold. At our highest value of E_{excess} HCO is still predominantly in its ground $v=0$ state. These results are consistent with the near threshold calculations of Cordeiro *et al.*⁵⁶ and Kurosaki and Yokoyama⁵⁷ who both suggest negligible vibrational excitation of the HCO fragment; indeed both calculations showed that the HCO fragment lost internal energy relative to its zero-point energy.

Our simulations indicate that significant vibrational excitation of the lowest-frequency umbrella mode in CH_3 , v_2 , is only possible at the highest excitation energy considered here, $E_{\text{excess}} = 24.4$ kJ/mol. These results are consistent with the findings of Kurosaki and Yokoyama,⁵⁷ who found that

the CH_3 fragment vibrational energy was less than its zero-point energy, indicating that the CH_3 fragments were formed with no vibrational excitation. In contrast, Cordeiro *et al.* predicted significant vibrational excitation of the CH_3 fragment,⁵⁶ which is inconsistent with our trajectory results.

2. Rotational distributions

We predict significantly lower average rotational energies for both the HCO and CH_3 fragments than the two previous trajectory studies.^{56,57} These discrepancies may be explained by the differences in the underlying potential-energy surfaces (UB3LYP vs RO-CCSD(T)), the small number of trajectories used in the direct dynamics studies, and the choice of whether or not to include zero-point vibrational motion in the trajectory simulation. The results of Cordeiro *et al.*⁵⁶ and Kurosaki and Yokoyama⁵⁷ are expected to be influenced by redistribution of internal energy from zero-point vibrational modes into the low-frequency transitional (rotational and translational) modes during the trajectory simulation.

3. Translational distributions

Our results would tend to predict higher average relative translational energies than those observed by Cordeiro *et al.*⁵⁶ and similar average relative translational energies to Kurosaki and Yokoyama.⁵⁷ The UB3LYP calculations used in both direct dynamics simulations underestimate the vibrationless reverse barrier height (Table I), but the different sampling techniques and the inclusion of zero-point energy (125 kJ/mol at the transition state⁵⁷) may considerably effect the dynamics.⁸⁷⁻⁹² As our PES is based on more accurate *ab initio* data and is explicitly constructed in terms of the C-C coordinate, we expect our results to provide the most accurate theoretical estimates of the relative translational energy of the product fragments to date.

C. The transition from impulsive to statistical dynamics

In the previous section we commented briefly that the shape of the HCO and CH_3 rotational distributions shifts from a symmetric Gaussian-shaped distribution at low energy to one that is more skewed and resembles a Boltzmann distribution at higher energy. These descriptors come from common descriptions of rotational distributions and are considered to arise from impulsive dynamics in the first case and statistical dynamics in the second case. Therefore the dynamics of the acetaldehyde reaction appears to shift from impulsive to statistical over this relatively small range in available energy, at least when the partitioning of the rotational energy is considered. It is this aspect of the dynamics of acetaldehyde photodissociation that we explore here: the changing nature of the distributions as a function of increased energy.

The interpretation of complex experimental data is aided by comparison with theory and/or simple statistical or dynamical models. The sophistication of the comparison can range from quantum wave-packet propagation on a full-dimensional PES for very small molecules²² to classical trajectories on an *ab initio* PES, such as used in this and other

studies on larger species.^{56–58,88–90} When increased complexity makes the development of a multidimensional PES impractical, reaction paths can still be calculated and much simpler models are used to interpret the experimental product energy distributions. These simple models can be loosely categorized as three types: statistical, impulsive, and hybrid. They correlate with three prototypical reaction coordinates: bound, repulsive, and barrier, respectively.

The acetaldehyde reaction on the triplet surface has a prototypical “barrier” reaction coordinate, with a “late transition state,” where the transition state structure is largely the structure of the products, and the impulse of the recoil in the exit channel is soft. A common experimental approach to interpret the dynamics on such a surface (and one used in several experimental papers on acetaldehyde^{41,46,47,51}) is to employ a hybrid model, where the available energy is separated into two reservoirs—the “impulsive reservoir,” which accounts for the energy distribution from the fixed exit channel dynamics, and the “statistical reservoir,” which arises from the strong mixing of states above the barrier and which results in a more statistical distribution of energy into the fragments.

The term statistical reservoir implies that the energy disposal by this mechanism should be statistical, both *within* a specific degree of freedom and *between* the degrees of freedom. It is rare in experiments on large molecules that information is available for all degrees of freedom (df). Frequently, reaction dynamics are interpreted based upon just one fragment, or only an average energy in different df, or measurements that are more sensitive to a particular type of product motion, e.g., translation. Experimentalists often attempt to infer the underlying dynamics of a reaction faced with such limited data and use these core models to compare with measured data and to predict how the missing df and/or fragments might behave.

We have shown above that our classical trajectory results are validated by many experimental results. A theoretical study such as this has the advantage that we can explore every df of both fragments at any energy. We can average the distributions and reduce the data to mimic reduced dimensionality experimental data in any reasonable way and use the common simple models to compare with the classical trajectory results. We start by examining the distribution of energy in each df and then consider the average energy distributed across the df.

The distribution of energy in the HCO rotational df has been subject to the greatest scrutiny of any df. Lee and Chen observed rotational distributions that were described as “Gaussian” and inferred the average rotational energy by direct averaging, rather than Boltzmann fitting.⁴⁶ Hanazaki and co-workers,^{49,51} Terentis *et al.*,⁴⁷ and Cruse and Softley⁴¹ all analyzed their experimental data assuming Boltzmann population distributions of rotational energy. The trajectory results shown in Fig. 4 to a large extent explain the difference in interpretation between the various experiments. Over the range of E_{excess} in this work, which was the same as the experimental studies, the shape of the HCO rotational distributions shifts from quite symmetric (Gaussian) at low excess energy to less symmetric, more “Boltzmann-type” at higher

FIG. 6. Natural log of the HCO population as a function of HCO rotational energy for three different excess energies E_{excess} (labeled in kJ/mol). The top panel shows the classical trajectory results and the lower panel shows experimental results, taken from Ref. 46.

energy. This effect is shown more clearly in Fig. 6 as a Boltzmann plot [$\ln(\text{population/degeneracy})$ versus rotational energy], where a Boltzmann population distribution would yield a straight line. Figure 6(a) indicates that the classical trajectory populations at $E_{\text{excess}}=6.8$ kJ/mol are non-Boltzmann. As E_{excess} increases the plot straightens until at $E_{\text{excess}}=24.4$ kJ/mol it is almost linear. Figure 6(b) plots the experimental results of Lee and Chen⁴⁶ at the same values of E_{excess} , that is, E_{excess} as quoted in Ref. 46 rather than in Table III. Again, at low energy, the population is non-Boltzmann, and a straight line Boltzmann population is achieved as E_{excess} increases to 24.4 kJ/mol. Our calculated CH_3 rotational population distributions follow a similar trend although there are no experimental data with which to compare.

The translational energy distributions never assume a statistical, Maxwell-Boltzmann distribution. They remain distinctly inverted over the range of excess energies studied here, which is in agreement with the experimental results.⁴¹ The translational energy release attributed to the effect of the exit channel is never redistributed as the exit channel barrier is exceeded; there is no significant redistribution of the impulsive component of the translational energy arising from coupling in the exit channel. As a result, fragments with little translational energy remain rare.

Clearly, the product state rotational distributions approach a statistical distribution more rapidly as a function of

FIG. 7. Amount of average energy partitioned into internal and external degrees of freedom of HCO and CH_3 as a function of excess energy E_{excess} . The average energy has been separated in an impulsive reservoir, which is determined by the fixed exit channel [panel (a)], and statistical reservoirs [panel (b)] that increase with increasing excess energy (see text).

increased energy than does the translational distribution. To explore further how the dissipation of excess energy changes between the df and whether the product state distributions from our trajectory study suit the description of “impulsive” and “statistical” reservoirs, we treat the product energies in the same way as would have been done experimentally. To obtain the impulsive reservoir contribution, we plotted the average energy in each df, from Table II, against E_{excess} and linearly extrapolated to $E_{\text{excess}}=0$. The extrapolated average product state energy at $E_{\text{excess}}=0$ was taken to be the energy distribution at threshold, that is, the energy-associated impulsive reservoir. This yielded a relative translational energy of 26.3 kJ/mol, HCO vibrational energy of 0.7 kJ/mol, CH_3 vibrational energy of 0.4 kJ/mol, HCO rotational energy of 0.5 kJ/mol, and CH_3 rotational energy of 0.2 kJ/mol, as reported in Table II. The threshold energy distribution is also shown graphically in Fig. 7(a).

For excitation above threshold, the contribution of the statistical reservoir was obtained by subtracting the impulsive reservoir energy contribution from the overall energy in each degree of freedom. These statistical reservoir energy contributions are shown as a function of E_{excess} in Fig. 7(b). As E_{excess} increases, the average energy in all modes increases approximately linearly and no single degree of freedom dominates in the way that translational energy did in the impulsive reservoir.

The simplest statistical model is the equipartition theorem, in which the energy is apportioned classically, according to the number of df. As the energies in our trajectory study are indeed classical, this is a reasonable starting point. Equipartitioning of energy can be applied either at the product configuration or at the transition state. The argument for equipartitioning energy at the transition state is the assumption that the vibrational modes of the transition state correlate essentially adiabatically with the products, that is, the product distributions reflect the statistical distribution of energy at the transition state.³⁶ At the transition state there are 14 bound vibrations and no rotation as our calculations were performed with $J=0$. The imaginary frequency correlates with one of the relative translational df of the products and has been accounted for in the impulsive reservoir. Of the 14 transition state vibrations, nine correlate with vibrational df in the products (three for HCO and six for CH_3), three with total rotational df (we assume 1.5 for HCO and 1.5 for CH_3), and two with relative translational df. We obtain a “hybrid” impulsive/statistical model by summing the energy associated with the impulsive reservoir with the statistical energy predicted using equipartition at the transition state. Results for this hybrid model at an excess energy of 24.4 kJ/mol are given in Table II.

The predicted partitioning is in broad agreement with the classical trajectory results at 24.4 kJ/mol. The rotational df are dominated by the statistical component whereas the translational df are dominated by the very large impulsive component; the statistical component never dominates translation. These two results are borne out by both the trajectory and experimental results, both in terms of the behavior of the average energies and more particularly the behavior of the energy distribution within each df, Figs. 4–6. The vibrational df are also dominated by the statistical component, consistent with the trajectory vibrational energy distributions, Fig. 3.

The hybrid model does show some differences from the trajectory and experimental energies, however. The relative energy partitioned into $\text{CH}_3(\text{vib})$: $\text{HCO}(\text{vib})$: $\text{CH}_3(\text{rot})$: $\text{HCO}(\text{rot})$, according to equipartition, should be in the ratio 4:2:1:1. The ratios shown in Fig. 7(b) are closer to 4:2:3:1. Clearly, the HCO rotation has approximately three times the energy predicted by equipartition. Interestingly, the average energy deposited into CH_3 rotation remains appropriate. This suggests that there is either continuing nonstatistical population of the HCO rotation above the barrier or coupling in the product channel or both. Overall, the hybrid model of photodissociation dynamics appears to have considerable merit in describing the behavior of the product distributions as excess energy is added to the reaction. The shift from a Gaussian distribution to a more Boltzmann-type distribution is explained. All df compete more equitably for the excess energy, even though the translational d.f. are >90% dominant at threshold.

V. SUMMARY

The dissociation of T_1 acetaldehyde has been modeled by performing classical trajectory simulations on a full-dimensional global potential-energy surface interpolated

from RO-CCSD(T)/cc-pVTZ(DZ) *ab initio* data along the minimum-energy path to reaction. At each initial excess energy E_{excess} , the CH_3 and HCO product vibrational and rotational energy distributions and the relative translational energy distribution were determined. These distributions and their averages were compared with previous experimental and theoretical results and were used to resolve a number of discrepancies in the previous studies.

A. The shape of the HCO angular momentum distribution

Previous experimental HCO angular momentum distributions have been fitted to both Boltzmann distributions (implying statistical dynamics)^{47,51} and a Gaussian (implying impulsive dynamics).⁴⁶ Our trajectory results illustrated (Fig. 4) a clear transition in the shape of both the HCO and CH_3 angular momentum distributions from a symmetric (Gaussian) distribution to a Boltzmann-type distribution as the value of E_{excess} increased from near threshold to 24 kJ/mol.

B. The average HCO rotational excitation

The experimental results of Lee and Chen⁴⁶ and Cruse and Softley⁴¹ suggest that the HCO rotational excitation increases with E_{excess} whereas the earlier results of Hanazaki and co-workers^{49–51} indicated that the HCO rotational excitation was constant as excess energy increased. Our classical trajectory results indicated a significant increase in HCO rotational excitation with E_{excess} consistent with Lee and Chen⁴⁶ and Cruse and Softley.⁴¹

C. CH_3 vibrational excitation

Lee and Chen⁴⁶ suggested that the CH_3 fragment may be born with significant vibrational excitation although Terentis *et al.*⁴⁷ inferred little vibrational excitation at $E_{\text{excess}} = 15.2$ kJ/mol and Cruse and Softley,⁴¹ observed excitation of the CH_3 umbrella mode only for $E_{\text{excess}} > 12$ kJ/mol. Furthermore the direct dynamics results of Kurosaki and Yokoyama⁵⁷ indicated no excitation of the CH_3 fragment whereas the simulations of Cordeiro *et al.*,⁵⁶ performed under similar conditions, yielded significant excitation. Our trajectory simulations indicate little vibrational excitation in the CH_3 fragment at $E_{\text{excess}} < 12$ kJ/mol ($E_{\text{avail}} < 36$ kJ/mol), consistent with Terentis *et al.*,⁴⁷ Cruse and Softley⁴¹ and Kurosaki and Yokoyama.⁵⁷ As the excess (or available) energy increases, we observed that excitation of the CH_3 umbrella mode becomes increasingly likely, in agreement with Cruse and Softley's experiments.⁴¹

In addition our trajectory results were consistent with a number of previous observations of the dissociation dynamics of T_1 acetaldehyde.

- The HCO fragment has significantly greater rotational energy than the CH_3 fragment.
- We see no vibrational excitation in the HCO fragment.
- The CH_3 fragment is formed with little rotational excitation but which increases as E_{excess} increases.

- The average relative translational energies of the HCO and CH_3 photoproducts agree semiquantitatively with the translational energy distributions obtained from experiment.

Our trajectory results were also interpreted in terms of simple models of impulsive or statistical dynamics. The energy in the vibrational, rotational, and translational degrees of freedom was partitioned into impulsive and statistical reservoirs. At threshold $>90\%$ of the available energy was partitioned into the relative translational motion of the products, indicating that the reaction at threshold is effectively impulsive and energy redistribution does not occur in the exit channel. The energy in the various degrees of freedom was found to increase approximately linearly with E_{excess} , in broad agreement with the equipartition of energy, indicating that the random partitioning of excess energy into the various degrees of freedom at the transition state is effectively conserved in the products. Thus, as E_{excess} increases, the reaction becomes increasingly statistical. The HCO rotational energy, however, was significantly larger than that predicted from an equipartition argument. This is brought about by continuing nonstatistical population of this df at the transition state and/or coupling in the product channel. The trend toward increasingly statistical behavior as E_{excess} increases is also reflected in the shape of the rotational distributions, which shift from a symmetric, Gaussian shape to a Boltzmann-type distribution. To our knowledge, this is the first time that a clear transition in an energy distribution from impulsive to statistical dynamics has been observed in classical trajectory simulations. This lends support to the experimental method of separating the dynamics into impulsive and statistical reservoirs and the use of hybrid models to interpret experimental distributions on PESs with a barrier.

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