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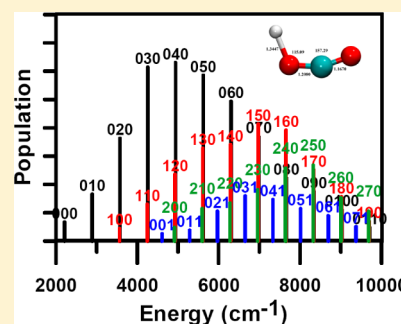
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ABSTRACT: Quasi-classical trajectory studies have been carried out for the HO + CO → H + CO₂ reaction and H + CO₂ inelastic collision on a recently developed global potential energy surface based on a large number of high-level ab initio points. The CO₂ vibrational state distributions for these processes have been determined using an original normal-mode analysis method. It was found that the CO₂ product of the reaction is highly excited in both the Fermi-linked bending and symmetric stretching modes, but little population was found in the antisymmetric stretching mode. The substantial excitation of the CO₂ vibration, while consistent with the geometry of the transition state in the exit channel, is in disagreement with available experimental data. For the inelastic collision, the CO₂ is much less excited despite much higher total energies. In addition, excitations in all vibrational modes were found, in good agreement with experiment.



I. INTRODUCTION

The HO + CO → H + CO₂ reaction is one of the most important combustion reactions.¹ This final step in hydrocarbon oxidation releases a large amount of heat but represents an important kinetic bottleneck because of its small rate constant. It also plays a role in the balance of the atmospheric OH concentration.² The kinetics of the reaction has been extensively investigated, and the rate constant is pressure-dependent and decidedly non-Arrhenius.^{3–5} In the low pressure limit, the rate constant is roughly the same value at low temperatures but rises exponentially above 500 K. This behavior is attributable to the unique complex-forming reaction pathway in this system,⁶ which has two bottlenecks.⁷ As shown in Figure 1, the bottleneck in the entrance channel (TS1) governs the formation of the HOCO intermediate, while the saddle point in the exit channel (TS2) controls the decomposition of HOCO into the product channel. The interplay between these two near-isoenergetic bottlenecks is responsible for the unusual behavior of the rate constant.

The dynamics of the reaction has also been investigated experimentally.^{8–13} Crossed molecular beam^{10,11} and real-time measurements^{14,15} indicated a relatively short lifetime for the HOCO intermediate. Translational energy distributions of the products suggested limited vibrational excitation in the CO₂ product,^{10,11} although few state-resolved experiments have been reported. In one experiment, Frost et al.⁹ used a tunable diode laser finding that the fraction of vibrational energy, $\langle f_v \rangle$, is only about 6% of the total energy available, so the CO₂ product is predominately in its (0,0,0) vibrational ground-state. The

excited CO₂ was found in bending excited states (0,*n*₂,0) with their Fermi-linked symmetric stretching excited states (*n*₁ = *n*₂/2,0,0). However, no absorption from the (0,0,1) level (antisymmetric stretching) was detected. Shi et al. reported significant excitation in the antisymmetric stretching mode of the CO₂ product.¹² The limited CO₂ vibrational excitation observed in experiment of Frost et al. is consistent with the translational distribution in the molecular beam experiment, which peaks near the highest accessible translational energy.^{10,11}

In sharp contrast to the scarcity of experimental work, there have been many theoretical studies on the dynamics of the title reaction,¹⁶ using both quasi-classical trajectory (QCT)^{17–21} and quantum mechanical (QM) methods.^{22–36} However, these studies have been hampered by uncertainties in the HOCO potential energy surface (PES), which was typically constructed with a small number of ab initio points.^{7,19,37–39} Among the various versions of the PES, the ones by Yu, Muckerman, and Sears (YMS),³⁸ by Lakin, Troya, Schatz, and Harding (LTSH),¹⁹ and by Valero, van Hemert, and Kroes (VvHK or Leiden)³⁹ have been widely used in dynamical studies. To remedy this problem, we have very recently developed^{40–42} a chemically accurate PES based on about 50 000 points at the

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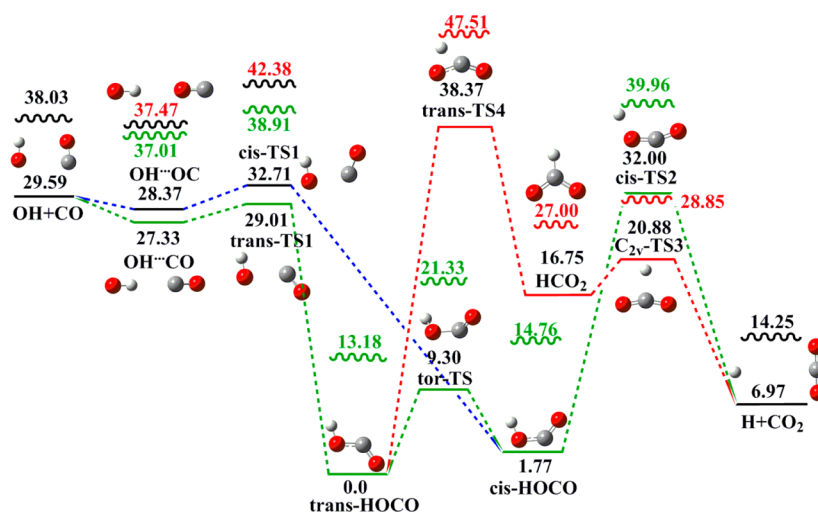


Figure 1. Energetics of the HOCO system. The OH + CO reaction leads to the formation of H + CO₂ via a complex-forming pathway involving both *cis*- and *trans*-HOCO complexes. The decay of the HOCO intermediates via TS2 (green) is the dominant pathway although the pathway via TS4 (red) might play a minor role as well. For H + CO₂ collisions, most reactive trajectories surmount the TS2 to enter the HOCO wells as well. The energies (kcal/mol) are given in reference to the *trans*-HOCO minimum. The curvy lines represent energies with ZPE corrections. Adapted with permission from ref 40. Copyright 2012 American Institute of Physics.

coupled-cluster singles and doubles and perturbative triples (F12 version) (CCSD(T)-F12/AVTZ) level, fitted using a permutation invariant polynomial method.⁴³ Both QCT^{40–42} and QM studies^{44,45} on this new PES have been reported, and the agreement with available experimental data has generally been improved over previous studies. However, significant discrepancies still exist. For example, the QCT translational energy of the H + CO₂ products of the HO + CO reaction is significantly lower than the experimental peak,⁴¹ suggesting too much excitation in the internal degrees of freedom of CO₂ ($\langle f_v' \rangle = 38\%$), as compared to the experimental value of 6%.⁵ Interestingly, the overestimation of the CO₂ vibrational excitation was also found on the YMS, LTSH, and Leiden PESs,^{21,34,36} with $\langle f_v' \rangle$ of 32%, 22%, and 22%, respectively. Unfortunately, our earlier QCT study⁴¹ did not calculate the vibrational state distribution due to difficulties in determining the vibrational quantum numbers in the CO₂ product. In this article, we report the determination of the vibrational state distribution of CO₂ from these trajectories using a normal-mode analysis method proposed recently.⁴⁶ Comparison with results obtained using the same method on other PESs²¹ is also given.

As discussed above, the significant vibrational excitation in CO₂ is inconsistent with available experimental observations. A possible origin of this discrepancy is errors in the PES, particularly in the exit channel. To test the reliability of the H + CO₂ region of the PES, we have also investigated here the inelastic collision between CO₂ and a fast hydrogen atom, using the same QCT method. Such processes have been extensively investigated by Flynn, Weston, and co-workers at a quantum state resolved level, using diode laser absorption spectroscopy.^{47,48} Theoretical studies have also been reported on a previous PES.⁷ Comparison with these experiments is important to validate the new *ab initio* PES, particularly in the H + CO₂ channel. We note in passing that the H + CO₂ collision also leads to the formation of HO + CO, which has been extensively studied by several groups^{49–55} including Wittig's pioneering work on the photoinitiated reaction in a van der Waals complex between HX (X = Br, I) and CO₂.⁵⁶

This publication is organized as follows. The next section (II) outlines the QCT method and the normal-mode analysis for the determination of the vibrational quantum numbers of CO₂, as well as the binning strategies. The results are presented and discussed in section III. The final summary is given in section IV.

II. THEORY

A. Quasi-Classical Trajectory for Reactive and Inelastic Scattering. Standard QCT calculations have been performed for both the reactive and inelastic scattering processes using VENUS.⁵⁷ The CCSD-2/d version⁴¹ of the HOCO PES was used. The trajectories were initiated with a 7.5 Å separation between HO and CO or between H and CO₂ and terminated when the trajectories reached the separation of 5.5 Å for H and CO₂ and 7.5 Å for HO and CO, respectively. The propagation time step was selected to be 0.11 fs. Exceptionally long trajectories were halted if the propagation time reached a prespecified value (9.9 ps). The maximal impact parameter (b_{\max}) was determined using small batches of trajectories with trial values. The scattering parameters (impact parameter, vibrational phases, and spatial orientation of the initial reactants) were selected with a Monte Carlo approach. The vibrational coordinates and momenta of CO₂ were sampled using a normal mode approach.⁵⁸ The gradient of the PES was obtained numerically by the central-difference algorithm.

B. Determination of Vibrational State Populations and the Binning Procedures. To assign a discrete quantum-like vibrational state to the outcome of a classical trajectory, we adopted the algorithm called NMA (Normal Mode Analysis) recently developed by our group,⁴⁶ where an original modification was made to the VENUS code. This choice was motivated by its lower computational costs compared to the fast Fourier transform method.⁵⁹ These two methods yield similar results.

Since VENUS uses a space-fixed frame, a change to a body-fixed frame was necessary for NMA to be carried out. So, these calculations were preceded by a rotation and translation of the molecule in order to maintain the orientation of the respective

reference equilibrium geometry (Q_o) for which NMA was performed. The basic idea of the NMA method is to project the final coordinates ($Q_R - Q_o$) and momenta (P_R) of the trajectories onto the respective normal-mode space. It is thus possible to calculate subsequently the kinetic, potential, and vibrational energies for each mode i ,

$$E_k^i = \frac{1}{2\mu} (P_R)_i^2 \quad (1)$$

$$E_p^i = \frac{1}{2} \omega_i (Q_R - Q_o)_i^2 \quad (2)$$

$$E_{\text{vib}}^i = E_k^i + E_p^i = \left(x_i + \frac{1}{2} \right) \hbar \omega_i \quad (3)$$

where μ is the reduced mass and ω_i is the eigenvalue of mode i . This calculation is performed for each trajectory, and the total energy is then averaged. Note that in these modifications the rotational motion of the polyatomic system is not considered, and therefore, the vibrational and rotational motions are treated independently. Moreover, since the harmonic approximation was used for this calculation, one could expect a breakdown of the procedure for highly excited states. Therefore, this approach suffers from anharmonicity at the high end of distributions, although it is unlikely to affect the main conclusions of this article.

Finally, from the vibrational energy (eq 3), the harmonic vibrational action x_i for each mode i (in the case of CO_2 molecule, one has four modes that correspond to the symmetric and antisymmetric stretching modes and to the two degenerate bending modes) can then be obtained. Harmonic vibrational actions in trajectories are obviously continuous numbers and therefore need to be quantized in order to confer a quantum spirit to the quasi-classical results.

However, in practice, the set of trajectories ending with exactly integer actions is negligible. The alternative is to assign a weight to each trajectory such that the closer the final actions to integer values, the larger the weight. Several procedures can be adopted for assigning statistical weights to trajectories based on their harmonic vibrational actions.⁶⁰

The first procedure is the standard binning (SB), or histogram procedure, in which each trajectory contributes with a weight of one to the quantum state (x_i) of the i th mode associated with the nearest integer (\bar{x}_i). In the SB procedure, each trajectory ending in the CO_2 molecule with vibrational actions in the interval $(\bar{x}_i - 0.5, \bar{x}_i + 0.5)$ contributes to the statistics with a weight of one, and all trajectories are taken into account.

The second procedure is the Gaussian binning (GB),^{61–66} where the weight assigned to the vibrational action value x_i is a Gaussian function of $x_i - \bar{x}_i$, that is, a Gaussian centered at the nearest (integer) state \bar{x}_i . It is also necessary to note that one trajectory only contributes to one quantum vibrational state. Thus, the Gaussian weight is characterized by a full width at half-maximum of about 10%, and therefore, the action values ranging from $\bar{x}_i - 0.05$ to $\bar{x}_i + 0.05$ are those that mainly contribute to the population of the level \bar{x}_i . As a consequence, it is often necessary to run roughly 10 times more trajectories per vibrational mode within the GB procedure than the SB one for the same level of convergence. So, for the CO_2 molecule with four degrees of freedom, one is led to run $\sim 10^4$ times more trajectories with the GB procedure.

The third procedure (developed in refs 67 and 68 and called here one-dimensional Gaussian binning (1GB) as in ref 60) obviates this problem by pseudoquantizing the total vibrational energy instead of the vibrational actions. In this case, the 1GB weight is a Gaussian function of the difference of the harmonic energies. The 1GB procedure needs much fewer trajectories than the GB procedure for the same level of convergence of the final results, and therefore, it allows significant computational savings.

III. RESULTS AND DISCUSSION

We have computed for the $\text{HO} + \text{CO}$ reaction 500 000 trajectories, each at two collision energies (8.6 and 14.1 kcal/mol). The parameters for these trajectories are identical to those published in our earlier work.⁴¹ The large number of trajectories is necessary due to the small cross-section for this reaction. In addition, 10 000 trajectories were computed for the $\text{H} + \text{CO}_2$ inelastic collision at 32.3, 37.8, and 55.0 kcal/mol of collision energies. The former two have the same total energies as those of the $\text{HO} + \text{CO}$ trajectories, while the last corresponds to the energy in the experiments of Flynn, Weston, and co-workers.^{47,48} To simulate the experimental conditions, the batch of trajectories at 55.0 kcal/mol were sampled with a rotational temperature of 300 K. The few reactive trajectories were discarded in the analysis of the CO_2 vibrational state distribution.

We begin by analyzing the reactive events, $\text{HO} + \text{CO} \rightarrow \text{H} + \text{CO}_2$. Given the relatively small number of reactive trajectories and the large number of open vibrational states, we ruled out the expensive GB approach in our calculations. Moreover, we tested the 1GB weighting scheme, but given the large number of populated states, the statistical errors were too large for all but the most populated states. Interestingly, we found that, for the most populated states, the differences between SB and 1GB methods were negligible, so that the SB scheme is adequate for the present reaction. This is presumably due to the large exothermicity of the reaction, which leads to extensive vibrational excitation in the CO_2 product. We also analyzed the convergence with respect to the number of reactive trajectories and found that the SB results are already converged, and therefore, a larger number of trajectories will not change the conclusion, having only a minor effect on the states with very low populations. Finally, in a previous study on this reaction, we showed²¹ that the SB and 1GB procedures yield similar populations.

Figure 2 plots populations for different vibrational states of CO_2 produced by the $\text{HO} + \text{CO}$ reaction at 14.1 kcal/mol. Vibrational quantum numbers are denoted by (n_1, n_2, n_3) , with n_1 for the symmetric stretching mode, n_2 the bending mode, and n_3 the antisymmetric stretching mode. It is clear that the bending mode of CO_2 is highly excited, with distributions extending to $n_2 = 11$ and peaks near $n_2 = 4$ –5. Some excitation in the Fermi-linked symmetric stretching mode is also apparent. However, excitation in the antisymmetric stretching mode is less pronounced, with at most one quantum excitation. Similar behavior is observed at a lower (8.6 kcal/mol) collision energy, as shown in Figure 3, where the populations shift somewhat to lower vibrational states.

The highly excited bending mode of the CO_2 product can be traced back to the bent geometry of the exit channel transition state (TS2). As shown in Figure 4, TS2 has a cis-configuration with an OCO angle of 157° . As a result, reactive trajectories that overcome this transition state experience significant forces

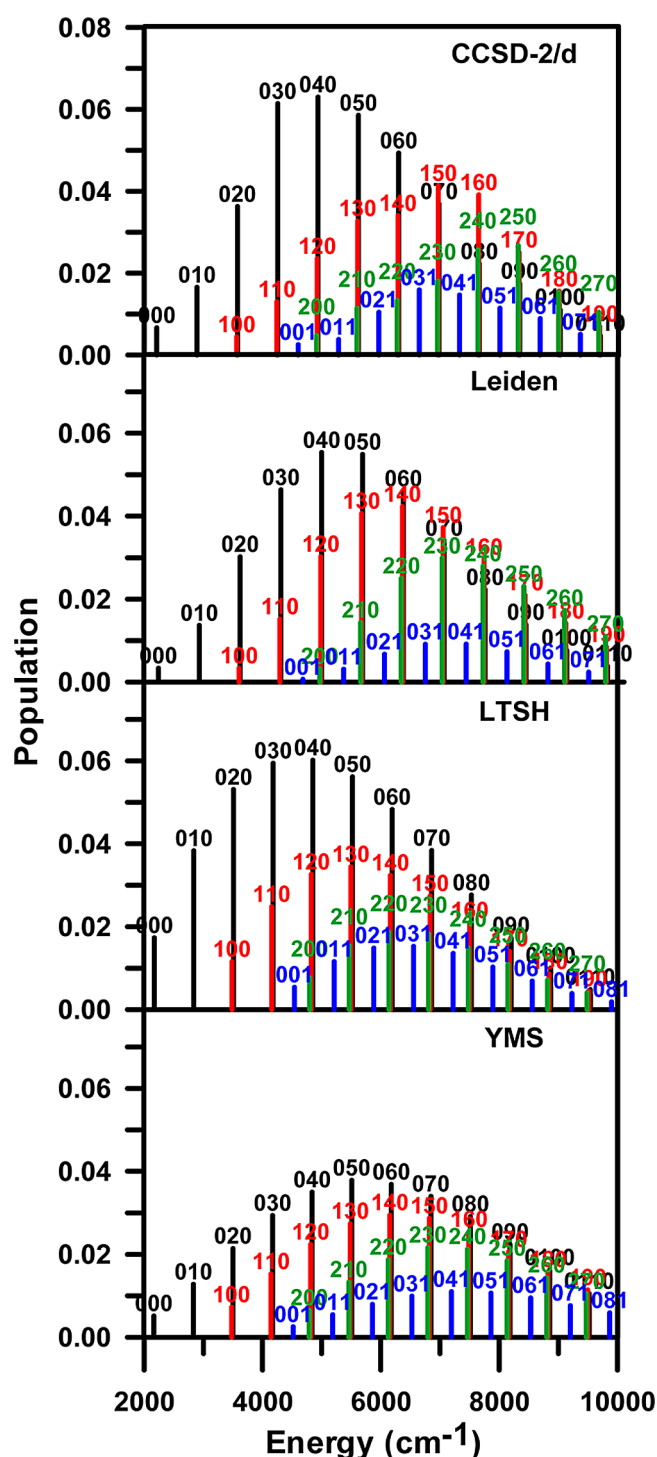


Figure 2. Vibrational state distribution of CO₂ resulted from the HO + CO reaction at the collision energy of 14.1 kcal/mol. The same distributions obtained on other PESs are also included for comparison. Note that only the most populated states are shown.

in the CO₂ bending degrees of freedom, resulting in vibrational excitation. The excitation in the stretching modes can be attributed to the elongated C–O bond length at the TS2. As discussed in our previous work,⁴¹ the CO₂ product is also excited in the rotational degrees of freedom, due to the torque exerted on the CO₂ molecule as H departs.

For comparison, the results obtained with other PESs are also shown in Figure 2. We can see that the new PES produces

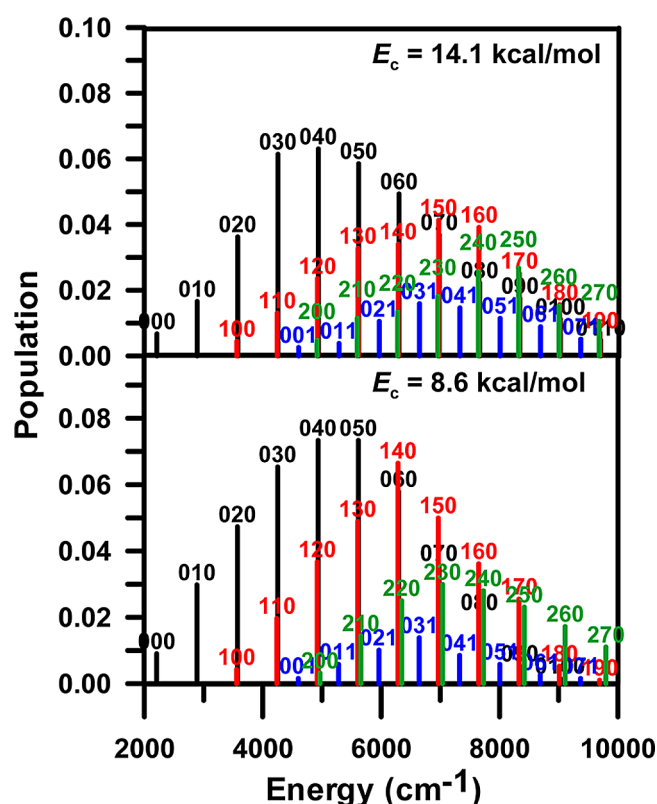


Figure 3. Vibrational state distribution of CO₂ resulted from the HO + CO reaction at the collision energy of 14.1 and 8.6 kcal/mol. Note that only the most populated states are shown.

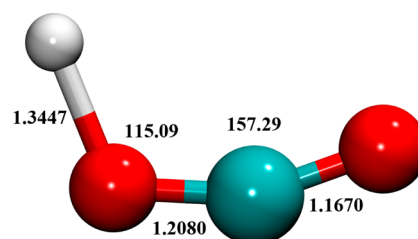


Figure 4. Geometry of the TS2 transition state. The bond lengths are given in Å and bond angles in degrees.

a CO₂ vibrational state distribution that is somewhat cooler than those on the Leiden and YMS PESs, and similar to that on the LTSH PES. The states with excited symmetric stretching mode are less populated on the current PES. As a result, the population is less scattered among the different vibrational states than in the older PESs. The QCT fraction of energy as vibration, $\langle f_v \rangle$, obtained with the new PES is 0.38, as compared with the results from previous surfaces: 0.32, 0.22, and 0.22 for the YMS, LSTH, and Leiden PESs, respectively.²¹ The similarity in the vibrational excitation patterns can be attributed to the similar transition state geometries obtained in all previous high level ab initio calculations. These results are consistent with earlier QCT distributions reported by Schatz and co-workers.^{18,19}

The small excitation in the antisymmetric stretching mode in our QCT calculations is inconsistent with the experiment of Shi et al.,¹² who reported significant excitation up to four quanta in this mode. Such an extensive excitation seems to be improbable given the small difference between the two C–O bond lengths at the transition state (TS2).

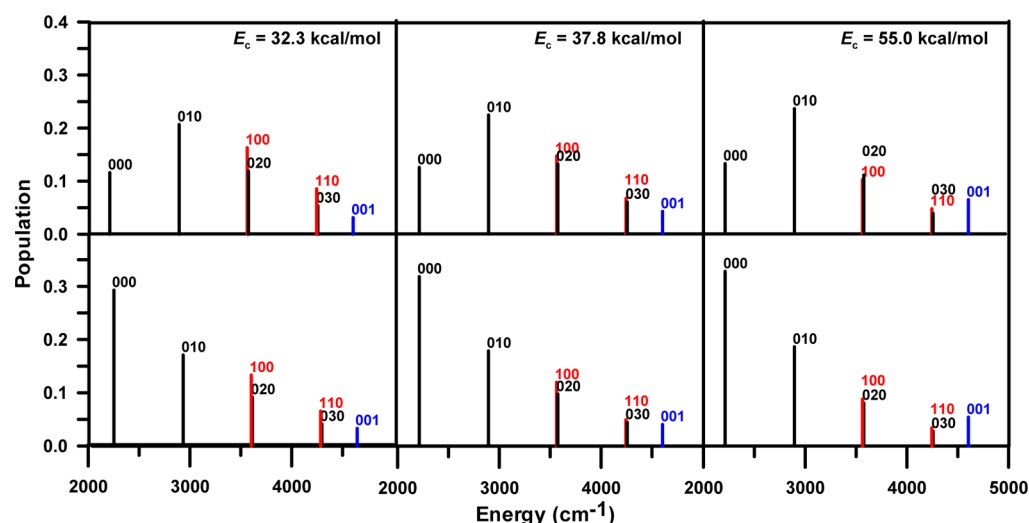


Figure 5. Vibrational state distribution of CO₂ resulted from the H + CO₂ collision at the collision energies of 32.3, 37.8, and 55 kcal/mol. Note that only the most populated states are shown.

However, the diode laser experiment of Frost et al.⁹ reported excitation only in bending mode up to $n_2 = 4$, but with most populations in the ground (55%) and first excited (0,1,0) states (25%). The other excited states all have populations less than 4%. As a result, only 6% of the total available energy are in the vibrational degrees of freedom. However, 10–11% were estimated from the translational energy distribution determined in a molecular beam experiment, with most available energy in the translational degree of freedom.¹¹ It is thus clear that the calculated vibrational excitation in the CO₂ product is significantly more intense than those experimental data. This picture is, however, inconsistent with the ab initio transition-state geometry of TS2, as discussed above. This significant discrepancy is puzzling, given the high level of the ab initio calculations used in determining the PES and, in particular, the dominant transition state (TS2) in the exit channel.

Very recently, a new global HOCO PES has been developed with a semiempirical density functional (MX06-2X) method.⁶⁹ In addition to a few new higher-energy transition states, the PES also yielded a monotonically increasing ICS via QCT for the H + CO₂ → OH + CO reaction, which gives a somewhat better agreement with experiment than our earlier QCT work.⁴² While the agreement with CCSD(T) data is good in stationary points, it is not clear, however, how reliable the functional is in describing other regions of the PES. No report on the reverse reaction has appeared yet on this new PES.

In addition to the PES, another factor that could contribute to a higher population of highly excited vibrational states is related to the well-known zero-point energy (ZPE) problem associated with QCT calculations.^{61–66,70–73} Although we have used pseudoquantization approaches to correct the QCT classical limitations, this criterion is applied only to the final product, not along the trajectory. Consequently, the conservation of the ZPE per mode is not guaranteed, allowing unphysical energy transfer between modes. However, we note that a recent full-dimensional QM calculation ($J = 0$) using the LTSH PES also found significant vibrational excitation in the CO₂ product, particularly in the Fermi-linked bending and symmetric stretching modes.³⁴ This QM result thus suggests that the vibrational excitation in CO₂ may not be due to the approximate treatment of the ZPE in the QCT calculations.

To validate the PES in the H + CO₂ channel, we have also determined the vibrational state distribution for the CO₂ molecule resulted from nonreactive collisions with H at three collision energies, and the results are presented in Figure 5. Note that for clarity, only the most populated states are represented, and as in the reactive events previously analyzed, the SB scheme was also used in this case. Since the ZPE effect could be significant due to the ineffectiveness in collisional vibrational energy transfer, we have determined the distributions with (upper panel) and without (lower panel) the imposition of a ZPE criterion that removes all ZPE violating trajectories in the products, i.e., we discard all trajectories with CO₂ vibrational energy below its ZPE where this criterion refers to the molecule as a whole. However, an equivalent criterion was not used for each mode, so that conservation of the ZPE per mode is not guaranteed. Finally, note that in the reactive events, the influence of the ZPE correction is negligible, i.e., practically all reactive trajectories finish with vibrational energy above the CO₂ ZPE.

It is found that some (about 30%) of the nonreactive trajectories are vibrationally elastic; in other words, they return to their vibrational ground (0,0,0) state of CO₂. This percentage increases slightly with collision energy, suggesting that the collision energy does not play a large role in vibrational excitation, at least in this energy region. When the ZPE violating trajectories (~25% of the total trajectories) are discarded, the percentage of elastic collisions drops from about 30% to about 12%, increasing the vibrationally inelastic collisions in a similar amount.

In the inelastic trajectories, the most populated state of CO₂ is the first bending excited state (0,1,0), with a percentage about 20%. The population of the (0,2,0) state represents about half of the (0,1,0) state. The excitation of the stretching modes is less probable. For example, at the experimental energy (55 kcal/mol), the population in the first symmetric stretching excited state (1,0,0) is similar to that in the (0,2,0) state, while the population of the antisymmetric stretch mode (0,0,1) is somewhat smaller than that for the (0,1,0) state.

The experimental ratios measured for the (0,0⁺,1), (0,1⁺,1), the upper and lower states of the Fermi-linked (1,0⁺,0)/(0,2⁺,0) pair, and (0,2⁺,0) states are 1.00:0.22:0.63:0.48:0.37.⁴⁸ If the populations for the (1,0⁺,0)/(0,2⁺,0) pair and (0,2⁺,0)

states, which cannot be distinguished in QCT calculations, are added together, the ratio for the $(0,0^{\circ},1)$, $(0,1^1,1)$, and the $(1,0^{\circ},0)/(0,2^{\circ},0)/(0,2^2,0)$ states are 1.00:0.22:1.48. These ratios can be compared with the QCT values of 1.00:0.54:3.12. The larger population in the bending excited states is understandable as broadsided collisions, which presumably result in bending excitations, are much more prevalent than head-on collisions, which lead to excitations in the antisymmetric stretch of CO_2 . The qualitative agreement with the experiments of Flynn, Weston, and co-workers strongly suggests that the $\text{H} + \text{CO}_2$ region of the PES is reasonable, which deepens the mystery for the surprising disagreement between the experimental and theoretical vibrational state distributions for the CO_2 produced by the $\text{HO} + \text{CO}$ reaction.

Collision between H and CO_2 also lead to significant rotational excitation. It was found by Flynn, Weston, and their co-workers that the rotational state distributions are essentially independent of the vibrational excitation and that they extend to $j = 70\text{--}80$ with peaks at $j = 40\text{--}50$.⁴⁸ In Figure 6, the

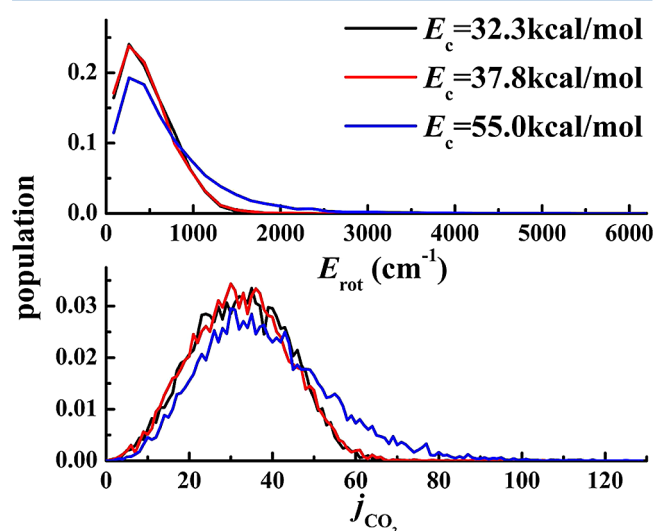


Figure 6. Rotational energy and state distributions of CO_2 resulted from the $\text{H} + \text{CO}_2$ collision at the collision energies of 32.3, 37.8, and 55 kcal/mol. All vibrational states were included, and the molecule was treated as a linear rotor.

calculated rotational state distributions in both energy and rotational angular momentum quantum number (j) are given. All vibrational states are included in calculating these distributions to improve statistics, and it is justified by the experimental observation that the rotational state distribution is largely independent of vibrational excitation. In reasonable agreement with the experimental observations, CO_2 is highly excited in the rotational degree of freedom. The peak positions increase with the collision energy but are somewhat lower than the experimental values, consistent with the somewhat hotter vibrational excitation discussed above.

IV. CONCLUSIONS

By normal-mode analysis of QCT trajectories, we have determined the vibrational state distributions for CO_2 produced by the $\text{HO} + \text{CO}$ reaction on a newly developed PES based on a large number of high-level ab initio calculations. The theoretical results predict significant excitation in the bending

mode along with some excitation in the Fermi-linked symmetric stretching mode. The vibrational excitation can be attributed to the bent geometry of the exit channel transition state (TS2), which is well established by numerous ab initio calculations on this system. In fact, QCT results on our new PES are qualitatively similar to those obtained on previous PESs. In addition, the possibility of overexcitation due to the QCT binning procedure is largely ruled out because quantum scattering calculations also found significant vibrational excitation in CO_2 .

It thus comes as a surprise that our latest theoretical predictions are still substantially different from the existing experimental data, which indicated much smaller excitation in the CO_2 vibrational degrees of freedom. The only state-resolved experiment reported that 6% of the available energy is channeled into CO_2 vibration, while the molecular beam experiment estimated that 10–11% of energy release is in the vibrational degrees of freedom for CO_2 . Since the former experiment was performed in a bulb, it is unclear if vibrational relaxation can be completely ruled out. However, the molecular beam experiment did not resolve the product vibrational states. At this point, the origin of the theory–experiment discrepancy remains unknown.

To examine the validity of the PES in the $\text{H} + \text{CO}_2$ region, we have performed extensive QCT calculations for the $\text{H} + \text{CO}_2$ collision. The vibrational state distribution of CO_2 is determined at three collision energies. In contrast to the reactive $\text{HO} + \text{CO}$ scattering, the nonreactive scattering yields CO_2 with much less vibrational excitation, even when the total energy is significantly higher than the exit channel transition state (TS2). The populations of low-lying vibrational states of CO_2 as well as the rotational state distribution are in reasonably good agreement with experimental results, suggesting an accurate representation of the $\text{H} + \text{CO}_2$ interaction potential.

The qualitative theory–experiment agreement for the nonreactive $\text{H} + \text{CO}_2$ scattering and the large discrepancy in the reactive $\text{HO} + \text{CO}$ scattering poses an interesting challenge for both theoreticians and experimentalists. We recognize that the inelastic collision between H and CO_2 may not sample exactly the same configuration space in reactive events, but the theoretical results are self-consistent. Despite many years of research, this seemingly simple system remains incompletely understood and more future work in both theory and experiment is needed.

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Notes

The authors declare no competing financial interest.

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