The dynamics of the $\text{H}_2 + \text{CO}^+$ reaction on an interpolated potential energy surface

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A potential energy surface that describes the title reaction has been constructed by interpolation of *ab initio* data. Classical trajectory studies on this surface show that the total reaction rate is close to that predicted by a Langevin model, although the mechanism is more complicated than simple ion-molecule capture. Only the $\text{HCO}^+ + \text{H}$ product is observed classically. An estimate of the magnitude of rotational inelastic scattering is also reported. © 2009 American Institute of Physics. [DOI: 10.1063/1.3156805]

I. INTRODUCTION

The CO^+ molecular ion has been observed in dense photon-dominated regions (PDRs) in interstellar and circumstellar environments.^{1–8} In PDRs the chemistry is dominated by photodissociation and photoionization and the subsequent reactions of the resulting radicals and ions. The abundance of CO^+ is significantly higher than suggested by modeling of the chemistry of these regions.⁷ Although Spaans and Meijerink⁹ suggested that the presence of x-ray radiation could explain the observed abundances in at least one object, neither the formation nor the destruction mechanisms of CO^+ is well understood, making the predictions of astrochemical models less precise.

The main routes to formation of CO^+ are proposed to be reactions of C^+ with OH and/or O_2 .¹⁰ Other possible sources of CO^+ are the reactions of O atoms with CH^+ (Refs. 11 and 12) and of CO with H_2^+ .¹³ In environments with an intense radiation source, giving high temperatures and a large degree of ionization, the charge-transfer reaction between H^+ and CO, and the direct photoionization of CO may contribute to CO^+ formation.¹ The former reaction is endothermic by 0.4 eV (Ref. 14) and the latter process has an ionization energy of 14 eV.¹⁵

CO^+ can be destroyed in collisions with the most abundant species in PDRs, i.e., H atoms, H_2 , and electrons.¹⁶ Therefore it seems unlikely that CO^+ will reach thermal equilibrium through collisional processes. Rather, the observed rotational transitions and the corresponding rotational distributions will retain a memory of the formation process. It is thus crucial to know the rates of destruction, especially their relative importance in comparison with the rotationally inelastic rates.

CO^+ is a precursor to HCO^+ ,^{13,17–20} which is also com-

monly observed in PDRs.^{10,21} HCO^+ is also believed to be the main precursor of CO, through dissociative recombination with electrons.^{20,21} The CO molecule is the second most abundant molecule in the interstellar medium after H_2 . The less abundant isomer HOC^+ is found in the same environments as HCO^+ , with abundances a factor of 10^2 – 10^4 lower than HCO^+ .^{5,22–24} The varying relative abundances are likely connected to the relative importance of different formation mechanisms of HOC^+ under different physical conditions.

The reactions that have been suggested to be the main sources of both HCO^+ and HOC^+ are

and

Reaction (1) has been extensively studied experimentally^{25–30} and the branching fraction of HOC^+ formation determined to be $6 \pm 5\%$.²⁸ Reaction (2) is the subject of the current study. Measurements of reaction (2) all agree that the rate constant is close to the Langevin capture rate constant (about $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$).^{17–19} This suggests that the reactivity is high and almost all collisions lead to reaction. Freeman *et al.* experimentally investigated the product branching ratios of reaction (2),¹⁷ concluding that the reaction leads to essentially equal amounts of HCO^+ (52%) and HOC^+ (48%) at room temperature. This has given support to the importance of reaction (2) as a possible source of HOC^+ .^{10,22} An alternative reaction that would lead predominantly to HOC^+ is $\text{C}^+ + \text{H}_2\text{O}$.^{17,31,32} Uncertainties in the abundance of gas-phase H_2O has made it difficult to estimate the importance of the latter reaction in this context.

Experimental and computational studies have inferred that inelastic and reactive processes are of roughly equal importance in collisions of CO^+ with electrons and H atoms. The rate constant of dissociative recombination of electrons

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and CO^+ is measured as $2.75 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at room temperature.³³ This is of the same order of magnitude as the largest rotationally inelastic rate constants of the same system calculated by Faure and Tennyson.³⁴ Measured rate constants of the $\text{H} + \text{CO}^+$ charge-transfer reaction lie in the range $(4.0\text{--}7.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$,^{18,35} which is around 1/4 of the rate constant for collisions. This suggests that total spin is conserved in the reaction and the singlet $\text{H}^+ + \text{CO}$ products are only formed through collisions on a singlet potential energy surface (PES). The triplet PES that also correlates with the $\text{H} + \text{CO}^+$ reactants should therefore be unreactive. This observation led Andersson *et al.*³⁶ to calculate rotationally inelastic rate constants for the collisions of H and CO^+ on the triplet PES.

Contrary to the cases of collisions with electrons and H atoms, there is nothing to suggest that there is any large survival rate of CO^+ in collisions with H_2 . Due to the large reaction rate constant, one would expect that the rotationally inelastic component of the outcomes of $\text{H}_2 + \text{CO}^+$ is quite small. However, since H_2 is likely to be the most abundant collision partner of CO^+ , even small inelastic rates may be important in determining the rotational state distributions.

To the authors' knowledge, there are no previous computational studies of the $\text{H}_2 + \text{CO}^+$ reaction. Moyano *et al.*³⁷ studied the interaction of H with HCO^+ and HOC^+ , which constitute the product channels of $\text{H}_2 + \text{CO}^+$. The goal of that study was to estimate the isomerization rate constant from HOC^+ to the more stable HCO^+ in collisions with H atoms. This is one of the processes that will determine the relative abundances of HOC^+ and HCO^+ in PDRs.

The aims of the present study are (i) to calculate the $\text{H}_2 + \text{CO}^+$ reaction rate constant, (ii) to study the branching ratios of HCO^+ and HOC^+ formation in this reaction, and (iii) to estimate the relative importance of rotationally inelastic collisions for the same system. This will serve as a complement to experiments and as input to the modeling of interstellar and circumstellar environments.

II. METHOD

A. Constructing the PES

The study of reactive or nonreactive chemical processes on a molecular level requires knowledge of the PES for the system considered. The nature of the PES can be probed either experimentally or by using *ab initio* quantum chemical calculations.

In this study the PES has been computed as a modified Shepard interpolation over a data set of *ab initio* points using the Grow methodology. The details of the Grow methodology have been presented previously,^{38–41} so only a brief description shall be given here.

In this work, the potential energy at some molecular configuration Z is given by the expression

$$E(Z) = \sum_{g \in G} \sum_{i=1}^{N_{\text{data}}} w_{g \circ i}(Z) T_{g \circ i}(Z). \quad (3)$$

In this equation, the sum over i iterates over the N_{data} geometries ("data points") at which *ab initio* calculations have

been performed to evaluate the potential energy and its first and second derivatives. The T are second order Taylor series expansions for the energy around each data point. The quantity w is a normalized weight function that is constructed to ensure an interpolation of the *ab initio* data.⁴¹ The subscript $g \circ i$ denotes that the quantity is for permutation g of data point i . G is the symmetry group of the molecule, generally the complete nuclear permutation group. Thus, the sum over G means that all permutationally equivalent geometries are included in the expansion, so the interpolated potential obeys the underlying permutation symmetry.

Starting from an initial set of data points distributed along the minimum energy path of reaction (2), configuration space was explored using quasiclassical trajectories (QCTs). The initial states for the trajectories were selected from the irrotational microcanonical ensemble for each fragment at the energy corresponding to the correct zero point energy, taken as 16.5 and 26.4 kJ mol⁻¹ for CO^+ and H_2 , respectively. The initial center of mass separation was 18.5 Å and the impact parameter selected from a linear distribution with a maximum impact parameter of up to 13.2 Å, depending on the relative translational energy. The trajectories were integrated according to the classical equations of motion with a velocity-verlet integrator using a time step of 0.01 fs.

Geometries were selected to be added to the *ab initio* data set based on measures of the quality of the interpolated potential along the paths traced by the trajectories.^{38–41} Periodically, after adding a number (~ 100) of data points to the data set, larger batches of trajectories were evaluated to assess the reaction probability according to the current interpolated PES. The process was iterated until the calculated reaction probability was deemed sufficiently converged, indicating that dynamically relevant regions of the interpolated PES were determined accurately.

The QCT reaction rates calculated using the interpolated PES can be compared to the rates determined from Langevin theory. According to this theory, structureless ion-molecule collisions interacting solely through the charge-induced dipole interaction form a collision complex and react with a cross section given by

$$\sigma(E) = \pi q \left(\frac{2\alpha}{E} \right)^{1/2}, \quad (4)$$

where E is the relative translational energy, α is the neutral species' polarizability, and q is the ionic charge.

B. *Ab initio* calculations

Ab initio calculations were carried out using the GAUSSIAN 03 package.⁴² As in the work of Moyano *et al.*,³⁷ calculations were initially performed at the QCISD/6-311G(d,p) level of theory. Indeed, after adding 495 data points to the interpolation selected from classical trajectories simulating the $\text{H}_2 + \text{CO}^+$ reaction, the 1404 data points calculated by Moyano *et al.* describing the H_2CO^+ , HCOH^+ , $\text{H} + \text{HCO}^+$, and $\text{H} + \text{HOC}^+$ regions of the PES were added to the data set, whereupon the grow procedure from the $\text{H}_2 + \text{CO}^+$ channel was continued. Similarly to Moyano *et al.*, the energies of the final 2536 data points were replaced with energies calcu-

FIG. 1. Optimized structures of the stationary points at the QCISD/6-311G(*d,p*) level are shown. Bond lengths are indicated in angstroms and angles in degrees.

lated at the QCISD level with a triple zeta basis set, keeping the derivatives calculated with the 6-311G(*d,p*) basis set. This triple zeta basis set comprised the basis functions from the cc-pVTZ basis set on the O and C atoms and the basis functions from the aug-cc-pVTZ basis set on the H atoms.

Moyano *et al.* confirmed that excitations of three electrons into virtual molecular orbitals (triple excitations) have little effect on the calculated energies. Thus using the QCISD method with triples corrections [e.g., QCISD(T) or QCISD-T (Ref. 43)] would not significantly alter the calculated energies, justifying the use of the computationally cheaper QCISD without triples correction in this work. This has previously been demonstrated for the HCO^+ PES.⁴⁴

III. RESULTS

A. General features of the PES

Optimized structures of relevant stationary points on the PES and calculated relative energies at the QCISD/6-311G(*d,p*) level are shown in Figs. 1 and 2, respectively. Energies calculated at the QCISD level with the triple zeta basis set are also shown in Fig. 2.

As indicated in Fig. 2, it was found that there were different reactive channels available depending on the orientation of the colliding fragments. If the hydrogen molecule approaches the carbon of the CO^+ fragment, the H–H bond can be broken without a barrier as a H–C bond forms. Along the minimum energy path, the other hydrogen atom remains loosely bound in a linear complex vw4. The loosely bound hydrogen atom can dissociate to form the HCO^+ product, or the system can undergo some rearrangement over small barriers to form H_2CO^+ , the most stable species on the PES. The

FIG. 2. The reaction scheme for $\text{H}_2 + \text{CO}^+$ is depicted. Relative energies of stationary points at the QCISD/6-311G(*d,p*) level are shown in kJ mol^{-1} , with the energy calculated using the triple zeta basis set given in parentheses.

potential minimum of this species lies more than 300 kJ mol^{-1} below the $\text{H}_2 + \text{CO}^+$ asymptote.

H_2CO^+ can directly form HCO^+ by dissociating one of the hydrogen atoms, which passes through a shallow potential minimum on the way. Alternatively, a hydrogen atom can migrate to the other end of the ion to form HCOH^+ . This requires surmounting an energy barrier 79 kJ mol^{-1} higher than that for dissociating a hydrogen atom (69 kJ mol^{-1} higher with the triple zeta basis set). From HCOH^+ , either hydrogen atom can dissociate to form HCO^+ or HOC^+ . The barrier to form HCO^+ lies at a similar energy to the $\text{H}_2\text{CO}^+/\text{HCOH}^+$ isomerization barrier. With HOC^+ lying at a substantially higher energy than HCO^+ , the barrier to dissociate the hydrogen attached to the carbon atom to form HOC^+ is around 90 kJ mol^{-1} higher than the barrier to form HCO^+ from HCOH^+ . The highest barrier on this minimum energy path to form HOC^+ via H_2CO^+ lies below the asymptotic energy of the $\text{H}_2 + \text{CO}^+$ entrance channel, suggesting that any formation of HOC^+ via this route does not require a substantial activation energy.

Note that Figs. 1 and 2, and the discussion above, refer specifically to *trans*- HCOH^+ . The *cis* form of HCOH^+ is also accessible, lying around 15 kJ mol^{-1} higher than the *trans*- HCOH^+ energy with a *cis*-*trans* isomerization barrier around 75 kJ mol^{-1} above the *trans*- HCOH^+ energy.³⁷ Hydrogen atoms can dissociate from *cis*- HCOH^+ to form HCO^+ and HOC^+ , with the energies of the saddle points being similar to those for reactions from *trans*- HCOH^+ .

H_2 can also react at the oxygen end of CO^+ . Two distinct reaction paths have been identified, largely depending on the orientation of the H_2 axis. If approaching with the H_2 axis roughly perpendicular to the CO^+ axis, the stable intermediate COH_2^+ can be formed directly via a saddle point of the order of 60 kJ mol^{-1} above the entrance channel energy, after passing through a very shallow potential minimum. A hydrogen atom can dissociate from COH_2^+ over a 147 kJ mol^{-1} barrier to form HOC^+ .

On the other hand, if the two diatomics approach roughly collinearly, then HOC^+ can form with a mechanism

analogous to the direct formation of HCO^+ via vw_4 , discussed above. Unlike the barrierless carbon-end reaction, however, breaking the H_2 bond to form $\text{H} + \text{HOC}^+$ requires passing over a barrier at saddle point TS_5 . This saddle point was calculated to be 46 kJ mol^{-1} above the reactant energy at the QCISD/6-311G(*d,p*) level. This barrier drops to 24 kJ mol^{-1} with the triple zeta basis set used in this work.

In the absence of other information, Fig. 2 may lead one to conclude that in low temperature $\text{H}_2 + \text{CO}^+$ collisions the primary product would be $\text{HCO}^+ + \text{H}$. As well as the simple barrierless path from the reactants to this product via vw_4 , there are two more paths to this product (through the H_2CO^+ well) on which the highest barrier lies 100 kJ mol^{-1} or more below the reactant energy. In a dense environment collisional stabilization may lead to the formation of significant amount of H_2CO^+ or HCOH^+ , but this is unlikely to be relevant to astrochemical applications. The remaining reactive product channel to $\text{HOC}^+ + \text{H}$ can occur without activation as there is a path to this product along which the highest barrier lies below the entrance channel energy. However, this path requires a complicated sequence of rearrangements which are unlikely to occur before dissociation into other channels. Moreover, one would expect the energetic differences between the paths to strongly favor the HCO^+ product channel. The other paths to HOC^+ (via COH_2^+ or vw_3) cannot occur without tunneling at low temperatures. Note that the isomerization barrier from HCO^+ to HOC^+ lies substantially above the entrance channel energy,³⁷ although it is thought that interactions with other neutral species can reduce the barrier height of this isomerization.^{45–47}

B. $\text{H}_2 + \text{CO}^+$ reaction rate

An important aspect of the grow methodology is monitoring derived dynamical quantities as points are added to the *ab initio* data set defining the interpolation. An example of the convergence of the total reaction cross section with increasing data set size is shown in Fig. 3, calculated from batches of at least 1500 trajectories with an initial relative translational energy of 0.41 kJ mol^{-1} . The error bars indicate one standard error either side of the calculated value. This figure shows that adding the final several hundred data points (out of the total of 2563 data points) did not alter the calculated cross section within the estimated uncertainty. These results are typical of calculations at higher translational energies.

As discussed in more detail below, the only reaction product observed in the QCT calculations of this work was $\text{HCO}^+ + \text{H}$.

Figure 4 shows the total reaction cross section as a function of relative translational energy, calculated from the final 2563 data point interpolation of the QCISD/6-311G(*d,p*) PES. As expected for a barrierless ion-molecule reaction, the reactive cross section was found to decrease with increasing translational energy. The QCT reactive cross sections were found to agree quite well with the Langevin cross section calculated with the QCISD/6-311G(*d,p*) H_2 polarizability of $0.429 \text{ \AA}^3$, also shown in Fig. 4, particularly at translational energies greater than 1 kJ mol^{-1} .

FIG. 3. The calculated total cross section at a translational energy of 0.41 kJ mol^{-1} is shown as a function of the size of the *ab initio* data set (with data points in the order originally added to the set). Error bars show one standard error.

Some insight into the nature of the agreement between the QCT and Langevin cross sections is provided by Fig. 5. This figure shows the calculated reaction probability as a function of impact parameter for a number of translational energies.

As expected, and as in the Langevin capture model, the maximum impact parameter at which reaction occurs in the QCT calculations decreases with increasing energy. This is

FIG. 4. The total reaction cross section is shown as a function of the relative kinetic energy. QCT results from the original QCISD/6-311G(*d,p*) PES (■) and from the PES with the energies replaced by those calculated with the triple zeta basis set (●). Single standard error uncertainties are similar to the symbol size. The Langevin cross sections using the H_2 polarizabilities calculated at the QCISD/6-311G(*d,p*) and QCISD/aug-cc-pVTZ levels are shown as short and long dashes, respectively.

FIG. 5. Reaction probability is shown as a function of impact parameter for $\text{H}_2 + \text{CO}^+$ collisions at relative kinetic energies of 0.41 kJ mol^{-1} ($\blacktriangle$), 1.24 kJ mol^{-1} ($\circ$), and 2.49 kJ mol^{-1} ($\blacksquare$). The error bars show a single standard error uncertainty. The Langevin critical impact parameters b^* at these energies are 7.35 , 5.56 , and $4.65 \text{ \AA}$, respectively, each indicated by a vertical dotted line.

consistent with the $\text{H}_2 - \text{CO}^+$ interaction being primarily attractive at long range. However, unlike in the charge-induced dipole potential of the Langevin model, the real intermolecular potential exhibits repulsive regions. This manifests as nonunit reaction probability for low impact parameters. All of the QCT calculations performed in this work exhibited this behavior to some degree. As the translational energy is decreased, “steering” effects appear to allow the repulsive regions of the PES to be avoided leading to an increase in the reaction probability toward unity, as demonstrated by the results for the three energies in Fig. 5. At the lowest energy considered in this work there was still a substantial reduction in the reaction probability at low impact parameter, although the nature of the impact parameter sampling led to large uncertainties in the calculated impact-parameter-resolved reaction probabilities.

In the Langevin model the reaction probability is unity for all impact parameters below a critical impact parameter b^* and zero for all impact parameters above this value. The QCT reaction probabilities calculated from the interpolated potential varied from this behavior in two respects. First, the reaction probability at low impact parameters was significantly below unity, as discussed above. This would decrease the reaction cross sections below the Langevin value. Second, the reaction probability reduced to zero at impact parameters substantially ($\sim 2 \text{ \AA}$) above the Langevin b^* . This implies that the interpolated potential cannot be well represented by a one dimensional ion-induced dipole potential in the vicinity of the important centrifugal barrier region for a typical trajectory. Even a small increase in the impact parameter at which the reaction probability drops to zero substantially increases the calculated reaction cross section, as the cross section is proportional to the integral of the probability $P(b)$ multiplied by b . These two effects approximately cancel in the $\text{H}_2 + \text{CO}^+$ QCT calculations performed in this work,

leading to reaction cross sections in agreement with the Langevin model despite the substantial mechanistic differences.

The observed underestimation of the maximum reactive impact parameter by the Langevin value b^* cannot be rationalized by assuming that steering effects increase the effective polarizability of H_2 . The low moment of inertia of H_2 means that torques associated with the induced H_2 dipole will have an effective tendency to orient the H_2 internuclear axis toward the CO^+ fragment in the classical trajectories, making the effective polarizability shift from the rotationally averaged value to the slightly larger value parallel to the axis. However, the b^* calculated with the larger polarizability parallel to the axis is only on the order of 5% larger than those from the rotationally averaged polarizability shown in Fig. 5.

At the ranges important to determining the threshold maximum impact parameter, the potential will be well described by electrostatic and induction terms. In similar H_2 -cation capture reactions, the quadrupole moment of H_2 has been shown to be unimportant.^{48,49} This leaves interactions with the CO^+ permanent dipole as the dominant interaction neglected by the Langevin model. A simple analysis shows that the potential felt by a polarizable entity interacting with a charged species that has a permanent dipole of magnitude μ is given by

$$V(R) = -\frac{\alpha q^2}{2R^4} - \frac{2\mu\alpha q}{R^5} \cos \theta - \frac{\mu^2 \alpha}{2R^6} [1 + 3 \cos^2 \theta], \quad (5)$$

where θ is the angle between the dipole and the intermolecular axis. The first term is the only one present in the standard Langevin treatment. The second term accounts for interactions between the CO^+ dipole and the H_2 dipole induced by the CO^+ charge. This term averages to zero over orientations of CO^+ . The third term, accounting for the dipole-induced dipole interaction, does not average to zero, resulting in an average net attraction. Thus it is likely that this dipole-induced dipole interaction is primarily responsible for the larger maximum reactive impact parameter. Note also that the second and third terms of Eq. (5) vary with orientation at a given R , which may contribute to “softening” the drop of the reaction probability with increasing impact parameter.

We note in passing that, despite the presence of a deep well on the PES (corresponding to the formaldehyde cation), no long-lived trajectories were observed.

As indicated in Fig. 2, performing QCISD calculations with the triple zeta basis set gave substantially different energetics to using the 6-311G(*d,p*) basis set. However, the difference in the energies relative to the $\text{H}_2 + \text{CO}^+$ asymptote changed reasonably slowly with the geometry. For this reason only the energies at the data points were replaced with the energies from the larger basis set. The computationally demanding first and second derivatives required for the Taylor series expansions of Eq. (3) were retained at the values calculated with the 6-311G(*d,p*) basis.

The total reaction cross sections calculated with this energy-substituted interpolated PES are also shown in Fig. 4. The QCT cross sections on this PES are clearly larger than those calculated for the 6-311G(*d,p*) PES. This difference

can be readily rationalized as differences in the description of the H_2 molecule. (Note that a large part of the energy differences for the different basis sets evident in Fig. 2 came from breaking the H_2 bond.) Despite the differences identified above and evident in Fig. 4, the interpolated PES is grossly similar to the ion-induced dipole potential at long range. The isotropic polarizability of H_2 calculated at the QCISD/6-311G(*d,p*) level ($0.429 \text{ \AA}^3$) is substantially different to the $0.774 \text{ \AA}^3$ value calculated at the QCISD/aug-cc-pVTZ level that is relevant to the more accurate triple zeta calculations performed here. This triple zeta value is very near the QCISD basis set limit. Using the larger polarizability yields Langevin model reaction cross sections closer to the QCT values for the triple zeta energy-substituted interpolated PES. Similar trends are evident, with the QCT cross sections deviating more from the Langevin ones at lower translational energies.

The reaction cross sections $\sigma(E)$ can be related to the reaction rate constants at temperature T by

$$k(T) = \left[\frac{8}{\pi\mu(k_B T)^3} \right]^{1/2} \int_0^\infty E\sigma(E)\exp(-E/k_B T)dE, \quad (6)$$

where μ is the ion-molecule reduced mass and k_B is Boltzmann's constant. If the reaction cross sections are expressed as a power law $\sigma(E)=aE^\gamma$ (with $\gamma>-2$), the integral is easily evaluated to give the rate constant as

$$k(T) = a \left(\frac{8}{\pi\mu} \right)^{1/2} \Gamma(\gamma+2)(k_B T)^{\gamma+1/2}, \quad (7)$$

in which $\Gamma(x)$ is the gamma function. The QCT reactive cross sections shown in Fig. 4 for the triple zeta PES could be approximately fitted to the expression $\sigma(E)=(185 \pm 15) \times (E/1 \text{ kJ mol}^{-1})^{-0.60 \pm 0.05} \text{ \AA}^2$, so that $k(T)=(3.9 \pm 0.3) \times (T/1 \text{ K})^{-0.10} \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ as the most probable rate constant expression, where only the uncertainty in the prefactor has been considered. Taking into account the additional uncertainty in the exponent of the power law gives more realistic bounds of this expression as $k^+(T)=5.2(T/1 \text{ K})^{-0.14} \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and $k^-(T)=2.8(T/1 \text{ K})^{-0.06} \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. These rate constants vary from roughly $(2.9 \pm 0.6) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 20 K to $(2.2 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at 300 K. For comparison, Langevin theory gives a temperature independent rate constant of $1.50 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Similarly, the QCT cross section for the 6-311G(*d,p*) PES of $\sigma(E)=(130 \pm 10) \times (E/1 \text{ kJ mol}^{-1})^{-0.60 \pm 0.07} \text{ \AA}^2$ gives the most probable rate constant expression $k(T)=(2.8 \pm 0.2)(T/1 \text{ K})^{-0.10} \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The 20 and 300 K rate constants from this fit are $(2.1 \pm 0.6) \times 10^{-9}$ and $(1.55 \pm 0.15) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, respectively. The corresponding Langevin rate constant from the QCISD/6-311G(*d,p*) H_2 polarizability is $1.12 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

Figure 6 shows the internal energy distribution of the product HCO^+ ions. The data shown are typical of the distributions calculated in this work. The internal energies span a range of almost 200 kJ mol^{-1} , up to the 233 kJ mol^{-1} maximum allowed by the initial reactant energies. The distribution was found to be prominently peaked, with energies of

FIG. 6. The internal energy distribution of the HCO^+ product from QCT calculations with an initial relative translational energy of 0.41 kJ mol^{-1} is shown, relative to the equilibrium energy.

120–140 kJ mol^{-1} being the most common. This implies that on average around half of the 190 kJ mol^{-1} potential energy that is liberated by reaction to the HCO^+ channel of Eq. (2) becomes relative translational energy.

C. Product branching

Freeman *et al.*¹⁷ observed an almost equal mix of HCO^+ and HOC^+ in their room temperature H_2+CO^+ flow tube experiments. Furthermore, Smith *et al.*²⁰ interpreted the appearance of CH_5^+ in their chemically quenched ion trap experiments as being indicative of forming HOC^+ via Eq. (2). Contrary to these results, in this work not a single trajectory was observed to produce the HOC^++H product.

Examination of Figs. 1 and 2 reveals an explanation for why no HOC^+ was formed on the current PES, despite being energetically accessible. HOC^+ formation without surmounting an energy barrier substantially above the entrance channel energy requires first forming HCOH^+ . Following the minimum energy pathway to form HCOH^+ requires several changes in direction of the hydrogen atom that ends up bonded to the oxygen atom, relative to the heavy CO fragment. HCOH^+ cannot form directly from the reactants without passing over a barrier above the reactant energy. Rather, after initially forming HCO^+ with the other hydrogen atom in a loose linear ion-molecule complex, the hydrogen atom must migrate around the fragment before becoming covalently bound. During this process, the complex is highly vibrationally excited, having gained in the vicinity of 190 kJ mol^{-1} from the formation of the C–H bond. From most parts of this migration path the hydrogen atom can dissociate to form HCO^+ , climbing a very small potential energy hill to do so. Forming HOC^+ in this way is dynamically unlikely. Rather, it is much more probable that as the reactants approach the H_2 bond is broken and a C–H bond is formed. The remaining hydrogen atom is then ejected, forming the HCO^++H product.

However, these QCT calculations cannot rule out conversion from HCO^+ to HOC^+ after the main reactive collision. There are a number of processes by which this is possible, including inelastic or reactive interactions with some third body. In astrochemical contexts, tunneling through the isomerization barrier cannot be ruled out, as the HCO^+ formed is highly vibrationally excited (Fig. 6). On the internal energy axis of Fig. 6, the HOC^+ potential minimum and zero-point-corrected energies lie at 167 and 191 kJ mol^{-1} , respectively. These are well below the high energy limit of the distribution, meaning HOC^+ vibrational states are energetically accessible via tunneling from some HCO^+ product states. Note that on this scale the classical isomerization barrier lies above 320 kJ mol^{-1} .^{37,44}

The HCO^+ to HOC^+ tunneling rate can be estimated by considering tunneling through an Eckart barrier. Using high accuracy information about the transition state⁴⁴ gives a transmission probability through an appropriate asymmetric Eckart barrier⁵⁰ of the order of 10^{-16} . Multiplying this probability by the bending frequency of HCO^+ yields an estimate for the tunneling isomerization rate at the highest HCO^+ vibrational energy (233 kJ mol^{-1}) around 10^{-3} s^{-1} . This rate estimate decreases around three orders of magnitude for every 10 kJ mol^{-1} reduction in the HCO^+ energy.

D. Inelastic scattering

Energy transfer processes in nonreactive $\text{H}_2 + \text{CO}^+$ collisions are of interest for modeling CO^+ rotational evolution in interstellar and circumstellar regions. A detailed investigation of inelastic scattering in $\text{H}_2 + \text{CO}^+$ collisions is beyond the scope of the current work. However, it is useful to probe the current interpolated PES to test its suitability for more extensive inelastic scattering studies.

To that end, in this work we examine a measure of inelastic scattering in the QCT calculations, namely, the cross sections for producing CO^+ in a number of different rotational states. Examination of Fig. 5 shows that nonreactive trajectories were almost exclusively high impact parameter trajectories. Low impact parameter trajectories were disfavored both by the sampling of impact parameters and by reaction probabilities lying in the range of 0.5–1.0 at impact parameters below 6–10 Å (depending on the translational energy).

Figure 7 shows the calculated final average classical angular momentum as a function of impact parameter, for large impact parameters, calculated with different numbers of data points defining the PES. The CO^+ fragment was initially irrotational. This figure indicates that the average angular momentum of CO^+ after collision, for large impact parameter collisions, does in some sense converge as the size of the data set increases. The average final angular momentum falls with increasing impact parameter, at large values of the impact parameter, as expected. However, the final average CO^+ angular momentum remains nonzero even at impact parameters greater than 13 Å.

At such large impact parameters and at the energies considered in this work, the standard charge-induced dipole Langevin model predicts that the fragments will not ap-

FIG. 7. The final average angular momentum of CO^+ in nonreactive collisions is shown as a function of the impact parameter. The initial translational energy was 2.49 kJ mol^{-1} and the CO^+ fragment was initially irrotational. Results are shown for QCT calculations on PESs interpolating from 1300 to 2536 *ab initio* points.

proach closer than about 10 Å. Taking this model prediction as indicative, in this region torques on the CO^+ fragment are dominated by long range interactions; primarily the interactions of the CO^+ dipole and charge (offset from the center of mass) with the H_2 induced dipole. To quantify the quality of the interpolation in these regions, the interpolated PES was evaluated at a series of geometries as the CO^+ fragment was rotated relative to the H_2 molecule at long intermolecular distances. These interpolated energies were compared to *ab initio* energies at these geometries. Absolute errors of the order of 0.05 kJ mol^{-1} were found in the interpolated potential, making the dependence of the energy on CO^+ rotation completely spurious at some H_2 orientations. These errors are of the order of the spacing between the CO^+ $J=0$ and $J=1$ rotational levels. Thus one cannot rely on the interpolated PES for investigating these small angular momentum transfers at long range. Note, however, that at certain H_2 orientations the potential energy is much more strongly dependent on the CO^+ rotation angle, and these stronger oscillations are well reproduced by the interpolated PES. Thus large rotational energy transfers may be well described by classical dynamics on the interpolated PES.

Figure 8 presents cross sections calculated for angular momentum transfer to the initially irrotational CO^+ fragment as the data set size was increased. The classical final angular momentum was binned into integer J levels for the calculation of cross sections. It can be clearly seen that the final $J=1$ cross section is not particularly well converged as the *ab initio* data set increased in size and that these cross sections were comparable in magnitude to the reactive cross sections shown in Fig. 4. On the other hand, the calculated $J=2$ and $J>2$ cross sections were much more stable as data points were added to the interpolation. As discussed above,

FIG. 8. Total rotationally inelastic cross sections are shown as functions of the size of the data set for different final values of $J(\text{CO}^+)$. Cross sections are shown for final values of $J=1$ (solid line), $J=2$ (dashed line), and $J>2$ (dotted line). The initial relative translational energies were 0.41 kJ mol^{-1} (upper plot) and 2.49 kJ mol^{-1} (lower plot). Error bars indicate a single standard error uncertainty. $J=1$ results are considered unreliable.

the $J=1$ cross sections are considered to be unreliable and significantly too large, whereas the $J=2$ and $J>2$ cross sections are considered more reliable.

The interpolated PES with the 6-311G(d,p) energies replaced with triple zeta *ab initio* energies gives a better description of the overall shape of the PES in the capture region of the potential. However, on this PES spurious corrugations were larger due to the slight mismatch between the energies and derivatives defining the Taylor series in Eq. (3). Examining inelastic scattering quantities in QCT calculations on this PES revealed that significant energy transfers occurred even for collisions with initial impact parameters greater than 13 Å . These energy and angular momentum

transfers were much larger than shown in Fig. 7 for the PES calculated consistently using the 6-311G(d,p) basis set and did not converge as the data set size increased. We consider this PES inappropriate for inelastic scattering studies.

IV. DISCUSSION AND CONCLUSION

The best QCT estimate of the room temperature rate constant reported here, $(2.2 \pm 0.2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, is in reasonable agreement with the measured value of $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.^{17,18} The QCT calculations did not include a thermal average of the initial rotational states of the reactants. This may contribute to an overestimation of the rate constant due to the relatively small rotational constant of CO^+ (allowing many rotational states to be populated at low temperatures) and the presence of repulsive regions in the intermolecular part of the PES.^{51,52} The total reaction cross sections at the energies considered here are also in reasonable agreement with the values reported by Knott *et al.*¹⁹ These authors reported that the cross section decays more slowly than $E^{-1/2}$. However, the much smaller range of energies considered herein precludes any sensible comparison of the energy dependence of the cross section.

As pointed out above, not a single trajectory was observed to enter the $\text{HOC}^+ + \text{H}$ product valley. This is in strong contrast with the flow tube results of Freeman *et al.*¹⁷ and the ion trap results of Smith *et al.*,²⁰ both of whom observed evidence for significant HOC^+ formation. The lack of formation of HOC^+ in the current QCT calculations is easily rationalized with respect to features of the calculated PES, as discussed above and evident from Fig. 2. Direct attachment of hydrogen at the oxygen end of CO^+ requires crossing a substantial energy barrier, while migration of a hydrogen atom from reaction at the carbon end of CO^+ is dynamically unfavored. We cannot rule out HOC^+ formation via a tunneling mechanism; such an effect cannot be modeled with the classical dynamics used in this work. One possible tunneling mechanism is isomerization of vibrationally excited HCO^+ . However, the estimated HCO^+ isomerization rate at the highest HCO^+ internal energy is low and less than 25% of the HCO^+ product was formed at energies above the HOC^+ potential energy.

The significance of the nonformation of HOC^+ in reaction (2) in astrochemical contexts is quite profound. It will now be necessary to evaluate the importance of alternative formation routes, such as the $\text{C}^+ + \text{H}_2\text{O}$ reaction. As discussed in Sec. I this will be strongly dependent on the abundances of H_2O in regions of space where carbon is mostly ionized. Considering the barriers involved in reaction (2) much higher kinetic energies than studied in this work would be needed in order to form HOC^+ . Indeed, there are indications that CO^+ has a nonthermal translational energy distribution in the PDRs where it is observed. Black¹⁶ reported estimated average translational energies of about 25 kJ mol^{-1} . This is considerably higher than the average energies at the typical temperatures of a few hundred kelvins in these environments. This is not unexpected as the densities are extremely low and CO^+ is quite reactive. Since CO^+ could be formed with a “hot” translational energy distribution,³⁶ it would not

cool down efficiently before it is consumed in a reaction. Formation of some HOC^+ in reaction (2) under such conditions cannot be ruled out by the present study. Further experimental and computational kinetics studies are clearly needed to quantify the detailed rates of reaction (2) and related reactions that form HOC^+ and/or HCO^+ over a wide range of temperatures.

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