Preferential Isomer Formation Observed in $\text{H}_3^+$ + CO by Crossed Beam Imaging

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ABSTRACT: The proton transfer reaction $\text{H}_3^+$ + CO is one of the cornerstone chemical processes in the interstellar medium. Here, the dynamics of this reaction have been investigated using crossed beam velocity map imaging. Formyl product cations are found to be predominantly scattered into the forward direction irrespective of the collision energy. In this process, a high amount of energy is transferred to internal product excitation. By fitting a sum of two distribution functions to the measured internal energy distributions, the product isomer ratio is extracted. A small HOC+ fraction is obtained at a collision energy of 1.8 eV, characterized by an upper limit of 24% with a confidence level of 84%. At lower collision energies, the data indicate purely HCO+ formation. Such low values are unexpected given the previously predicted efficient formation of both HCO+ and HOC+ isomers for thermal conditions. This is discussed in light of the direct reaction dynamics that are observed.

In the past decades, astrochemistry has emerged as an essential discipline toward explaining the chemical composition of the early universe and drawing relations between interstellar chemical networks and the emergence of life.1–3 The importance of astrochemistry has increased with the number of detected molecules in the interstellar medium (ISM), whose present score is about 200 without counting isotopic substitution. While initially only low-mass species had been identified, the recent detection of large molecules such as polycaromatic hydrocarbons and fullerenes has opened new and exciting questions for the molecular astrophysics community regarding the formation, reactivity, and temporal stability of these species.4–6 An interplay between astronomical observations, theoretical models, and laboratory experiments is crucial in order to optimize and further propose astrochemical networks that contribute to the understanding of interstellar chemical abundances.

Besides radiative and surface processes, chemical reactions, and in particular ion–molecule reactions, are key processes influencing the composition of the ISM.7–11 Interstellar ion chemistry is commonly assumed to be initialized via cosmic ray ionization of molecular hydrogen. The formed $\text{H}_3^+$ rapidly undergoes a reaction with $\text{H}_2$ to form $\text{H}_4^+$, the most abundant molecular ion in space. The structure and reactivity of the trihydrogen cation has been thoroughly investigated throughout the years, as it is held responsible for the formation of many interstellar molecular ions due to the low proton affinity of $\text{H}_3^+$ and the resulting tendency to transfer a proton to many other atoms or molecules.12–17 Among the variety of chemical networks started by $\text{H}_3^+$, the reaction with the abundant CO molecule initiates the formation of crucial organic molecules such as alcohols, aldehydes, or carboxylic acids. In its first step, $\text{H}_3^+$ + CO can follow two competing reaction pathways:

$$\text{H}_3^+ + \text{CO} \rightarrow \text{H}_2 + \text{HCO}^+ \quad (\Delta_H = -1.76 \text{ eV}) \quad (1)$$

$$\text{H}_3^+ + \text{CO} \rightarrow \text{H}_2 + \text{HOC}^+ \quad (\Delta_H = -0.13 \text{ eV}) \quad (2)$$

The indicated reaction enthalpies ($\Delta_H$) have been taken from a recent theoretical publication.18 Reaction 1 produces the stable HCO+ ion, whereas formation of the metastable HOC+ through Reaction 2 is also possible. Both proton transfer reaction channels exhibit exothermic and barrierless character, whereby reaction 1 is considerably more exothermic. Each pathway proceeds via an intermediate ion-dipole complex that follows dissociation to the final products.19 The enthalpy difference between both channels amounts to 1.63 eV and is directly correlated with the difference in proton affinity of the carbon- and oxygen ends of CO.20 Proton migration between both isomers has to overcome a potential energy barrier, which, however, is known to be substantially lowered by the presence of a neutral catalyst that possesses a higher proton affinity than the O-side of CO.21,22

The formyl cation was astronomically detected in 197023 and has been the subject of many investigations, mainly due to its isomeric character.24–26 Formyl ($\text{HCO}^+$) and isoformyl (HOC+) cations are supposed to initiate different interstellar chemical channels, so that a deep understanding of their interplay and relative abundance is of fundamental relevance in order to model accurate chemical networks. In the last decades, many astronomical observations have obtained vastly different HCO+/HOC+ ratios between about 360 to 6000, thereby demonstrating a strong dependence of the relative isomer abundances on the specific chemical composition and evolution of the monitored region.27–31

The astronomical findings have stimulated theoretical and experimental investigations on the formation pathways of the
formyl and isoformyl ions. Recent theoretical works have shown high level electronic structure calculations of the stationary points along these two reactions. Other studies have analyzed the main forces involved in the interaction between $\text{H}_3^+$ and CO and have computed the reaction rate of each isomer channel as a function of temperature. These works predict a similar reaction rate for both isomer formations at conditions close to room temperature. Recently, molecular dynamics simulations on both the $\text{H}_3^+ + \text{CO}$ and the $\text{H}_2 + \text{HOC}^+$ reactions have been carried out, thereby predicting an efficient roaming mechanism to influence the isomer ratio.

Initial experimental investigations of the formation of the two isomers used indirect mass spectrometric techniques in order to estimate the HOC$^+$ abundance. Illies and co-workers obtained a 6% probability for HOC$^+$ formation in a collision-induced dissociation study. A study using an ion storage ring estimated an iso-formyl isomer abundance of 10% for the deuterated species following collision-induced dissociation. An additional proton migration pathway consisting of the H$_2$-catalyzed isomerization between the [H$_2$−HOC]$^+$ and the [H$_2$−HCO]$^+$ complexes has also attracted attention due to its possible influence on the HOC$^+$/HCO$^+$ isomer ratio. Smith and co-workers found a large rate coefficient for this reaction at 25 K and predicted a competition between HOC$^+$ isomerization and HCO$^+$ destruction through recombination processes to govern the relative isomer abundance. All these insights serve as a basis to understand the structure and energetics of the different isomer formation pathways. However, they lack an understanding of dynamical effects such as the influence of reactant preorientation or the inter- to intramolecular energy coupling and how it affects the reaction outcome.

This Letter presents the first experimental angle- and energy-differential relative cross sections for the reaction $\text{H}_3^+ + \text{CO}$. In particular, a kinematical distinction of both possible product isomers and an estimation of their branching ratio is pursued. For this purpose, an ion–molecule crossed beam apparatus is combined with velocity map imaging of the produced HCO$^+$ and HOC$^+$ ions. In the experiment, a pulsed H$_3^+$ beam formed in a pulsed plasma discharge is internally deexcited to approximately room temperature via buffer gas collisions in an octupole ion trap and subsequently crossed with a supersonic CO beam in the interaction region of a velocity map imaging spectrometer (see Methods section for details).

Mass 29 a.m.u. reaction products are extracted normal to the scattering plane and their three-dimensional velocity components are monitored by a position- and time-sensitive detector. Resulting raw velocity images are transformed into the center-of-mass frame. The upper panels in Figure 1 depict velocity images of the HOC$^+/\text{HOC}^+$ products formed by the $\text{H}_3^+ + \text{CO}$ proton transfer reaction. The arrows above the images indicate the relative velocity vectors of the reactants and the scattering angle $\theta$, the reactant velocities are also shown as black arrows in the images. The red and white dashed circles superimposed on the image describe the kinematical limits for HCO$^+$ and HOC$^+$ formation, respectively. Lower row: Product internal energy distributions associated with the depicted ion images. The internal energy describes the amount of initially available energy transferred into product internal degrees of freedom. The internal energy is shown with respect to the kinematical limit for HCO$^+$ formation. The gray bar indicates the region where only HCO$^+$ can be formed, whereas the green bar shows the energy range where autoisomerization can occur.

**Figure 1.** Upper row: Images showing the center-of-mass velocity distributions of HCO$^+$/HOC$^+$ products formed by the $\text{H}_3^+ + \text{CO}$ proton transfer reaction. The arrows above the images indicate the relative velocity vectors of the reactants and the scattering angle $\theta$, the reactant velocities are also shown as black arrows in the images. The red and white dashed circles superimposed on the image describe the kinematical limits for HCO$^+$ and HOC$^+$ formation, respectively. Lower row: Product internal energy distributions associated with the depicted ion images. The internal energy describes the amount of initially available energy transferred into product internal degrees of freedom. The internal energy is shown with respect to the kinematical limit for HCO$^+$ formation. The gray bar indicates the region where only HCO$^+$ can be formed, whereas the green bar shows the energy range where autoisomerization can occur. This Letter presents the first experimental angle- and energy-differential relative cross sections for the reaction $\text{H}_3^+ + \text{CO}$. In particular, a kinematical distinction of both possible product isomers and an estimation of their branching ratio is pursued. For this purpose, an ion–molecule crossed beam apparatus is combined with velocity map imaging of the produced HCO$^+$ and HOC$^+$ ions. In the experiment, a pulsed H$_3^+$ beam formed in a pulsed plasma discharge is internally deexcited to approximately room temperature via buffer gas collisions in an octupole ion trap and subsequently crossed with a supersonic CO beam in the interaction region of a velocity map imaging spectrometer (see Methods section for details).
limits represent the maximum center-of-mass speed allowed for the product ions given the collision energy and the respective reaction enthalpy. Thus, an event being scattered with velocities larger than the radius of the white circle can solely be ascribed to the HCO+ isomer.

At all relative collision energies, the product velocity distributions show dominant forward scattering, defined as scattering in the direction of the incoming CO molecule. Most of the product events are scattered into very low scattering angles, a fact that can be ascribed to a stripping-like process caused by high impact parameter collisions. The velocity of the product ions are clearly smaller than the center-of-mass speed of the incoming neutral molecule, showing a considerably high degree of internal excitation, a fact that has also been observed for related proton transfer reactions. This hints to an efficient coupling of the reaction coordinate to the rovibrational degrees of freedom of an intermediate ion−dipole reaction complex. The excess energy upon collision can be redistributed among the internal degrees of freedom of the HCO+/HOC+ and the H2 products. Due to the existence of multiple rovibrational modes, an ascription of the energy transfer to specific internal degrees of freedom is not evident from the experimental data.

From the velocity images, the distributions of the internal energies have been obtained (bottom panels in Figure 1). For all collision energies, high internal excitation is observed, with many events showing energies larger than the threshold for HOC+ formation. The ratio of the average internal energy to the total available energy, referenced to the rovibrational ground state of HCO+, is plotted in Figure 2 (left panel) as a function of the collision energy. Again, the relative internal energy fraction is substantial, above 0.5 for all collision energies, and is found to decrease slightly with increasing collision energy. This decrease does not depend on the scattering angle, as evidenced by the three dashed curves, which are derived by only considering the scattering angle ranges depicted in the right panel of Figure 2. The finding is in contrast to the pronounced scattering angle dependence of the internal excitation that has been detected for other ion−molecule systems in the collision energy range from 0.3 to 2.4 eV. Thus, the proton transfer dynamics in the present system does not depend significantly on the impact parameter.

As derived from the velocity images and the internal energy distributions, a direct separation of the distribution according to the two isomers can not be performed. At the lower collision energies a considerable fraction is clearly formed in the HCO+ isomer, including all events below the threshold for HOC+ formation indicated by the gray bars in energy distributions of Figure 1. The fraction that certainly amounts to the HCO+ isomer is 59%, 46% and 38% at 0.2, 0.6, and 1.8 eV, respectively. These values are lower limits for the fraction of this isomer. A better estimation of the isomer fraction is provided following a closer inspection of the internal energy distributions. In all graphs of the internal energy, only...
monomodal distributions are observed, which render it unlikely that all events beyond the threshold for HOC+ formation actually correspond to that isomer. In a resonant reactive collision without any energy transfer into internal degrees of freedom, each fragment would arrive at its kinematical cutoff, and the energy difference between both distributions would be equivalent to the difference in exothermicity between reactions 1 and 2 ($\Delta E = 1.63$ eV). Given the energy resolution of the experiment, this would lead to a distinctly bimodal internal energy distribution indicative of the formation of both isomer species. Assuming a similar energy loss for both isomer formation channels, the energy difference is reduced for increasing internal excitations. Thus, for substantial excitation an overlap between the energy distributions due to HCO+ and HOC+ formations can occur, leading to an effectively monomodal distribution.

In order to test the plausibility of two overlapping distributions for the two isomers, a fit to the energy distributions is performed. This fit is based on the assumption that the relative energy loss is equivalent for both isomer formation channels. Both isomer energy distributions are considered to follow a Gaussian velocity distribution with the same width. The fits were performed for collision energies up to 1.8 eV (details on the fit process are given in the Methods Section). At the two higher collision energies a substantial fraction of the internal energy distributions shows values above 3.57 eV, the energy limit for autoisomerization from HOC+ to HCO+. This region is shown by the green bars in the internal energy distributions of Figure 1 and corresponds to the regime where no specific isomer can be assigned.

Figure 3 depicts the fits to the product internal energy distribution for the three lower collision energies. At the 0.2 and 0.6 eV collision energies the fit yields a vanishing contribution of the HOC+ isomer with an upper limit that is estimated to be less than 10% (left and middle panels). The right panel shows the fit for 1.8 eV collision energy, which shows the presence of two overlapping product isomer distributions. The best fit yields a value of 13% ± 11% for the HOC+ fraction. Within this one-sigma accuracy, this essentially corresponds to an upper limit for the HOC+ fraction of 24% with a confidence level of 84%.

The width of the internal energy distribution depends on three main factors, namely, the uncertainty of the relative energy distribution given by the ion and neutral beam energy resolution, the spread induced by aberrations of the velocity mapping, and the intrinsic chemical dynamics, i.e., the difference in the energy partitioning for each reactive scattering event. Unfolding the respective broadening factors from the fit results yields the distribution caused by the intrinsic dynamics. It is found to follow closely the total fit function, whereas the technical accuracies contribute only slightly to the spread of the product energy distributions. Thus, the difficulty in distinguishing the two isomer channels is caused by the high excitation of product rovibrational degrees of freedom during the reaction.

The low HOC+ fraction contrasts with the trends proposed by different theoretical works, where a similar reaction efficiency is predicted for both isomer formation channels in a temperature range of 250–350 K. In particular, HOC+/HCO+ ratios between 0.4 and 0.6 are obtained at temperatures around 350 K by both Yu and Klippenstein, which correspond to HOC+ fractions of 0.29 and 0.37, respectively. Their results show a clear increase of this fraction with temperature, up to 350 K. Our experimental scattering experiments show a clearly lower HOC+ fraction, albeit at energies considerably higher than the ones considered in these simulations. This could imply that the trend of an increasing HOC+ fraction reverts at intermediate collision energies. It could also indicate that the internal excitation of the reactants, which in our case is at or below room temperature, plays a role for the branching.

One possible explanation for the extracted isomer fraction at the collision energies of the experiment builds on the effect of H2-catalyzed isomerization. Such a process should a priori involve the formation of an intermediate complex that supports overcoming the transition state barrier. However, the expected low-velocity isotropic scattering is not observed in the experimental data. Instead, the direct reaction process that is evidenced in Figure 1 may preferentially form HCO+ due to the charge-dipole interaction between H3+ and CO. Due to the higher electron density present at the carbon atom of CO, such an interaction steers the reactant preferentially toward a H–C orientation. In addition, the higher density of rovibrational states for the HCO+ geometry than for the HOC+ geometry also favor the transfer of the proton to the carbon end. Detailed chemical dynamics calculations will be very useful to investigate this further.

In conclusion, direct monitoring of the product angle- and energy distributions as a function of relative collision energy has allowed us to provide dynamical information for the key interstellar reaction H3+ + CO, albeit at collision energies higher than present in cold interstellar environments. Forward scattering dynamics of product HCO+/HOC+ ions, a high degree of product internal excitation independent of scattering angle, and a monomodal distribution of the product internal energy are observed at all collision energies. A two-component fit to the energy distributions provides an upper limit of 24% HOC+ with 84% confidence level for a scattering energy of 1.8 eV and of less than 10% for the two smaller collision energies of 0.2 and 0.6 eV. Given the observed direct mechanistic features in the measurements, the role of H2-catalyzed isomerization is considered rather improbable. Instead, preferential on-the-fly transfer of the proton toward the C atom, as well as preorientation of the reactants due to the long-range charge-dipole interaction could favor HCO+ formation.

Further studies will focus on reactions with monatomic neutral products, in particular H2+ + CO, in order to reduce the number of product degrees of freedom and thus possibly obtain a kinematical separation between both isomer products. Control of the H2+ vibrational population using laser ionization will allow us to monitor the effect of reactant internal excitation on the dynamics. These studies will provide further insight into the main factors influencing the HOC+/HCO+ branching ratio and thus add to the present experimental findings for this key astrochemical isomer competition.

**METHODS**

The experimental setup used in our group to study ion–molecule reactive systems is described in detail elsewhere. Therefore, only a brief description will be given here. The arrangement consists of a crossed beam apparatus combined with a velocity map imaging spectrometer. The whole experiment is operated at a repetition rate of 20 Hz. The reactant ions are produced by dissociative electron attachment to H2 in a pulsed plasma discharge source. H+, H2+, and H3+ are produced, extracted, and guided via a Wiley–McLaren-type
time-of-flight spectrometer toward an octupole radiofrequency ion trap, where H$_3^+$ ions are selectively stored. Thermal H$_3$ is introduced into the trap and collides with the incoming H$_3^+$, whereby a proton is likely being transferred from the internally excited ion to H$_2$, forming a new H$_3^+$. All H$_3^+$ ions are stored for tens of milliseconds in the trap and cool internally through further elastic collisions, before being extracted, decelerated and crossed with a supersonic neutral beam of pure CO at a relative collision angle of 60° in the interaction region of a differentially pumped scattering chamber.

The reactions’ collision energy is set by adjusting the H$_3^+$ translational energy. A typical ion beam energy spread of 350 to 400 meV (fwhm) is obtained. The velocity and translational temperature of the neutral reactants are determined by electron impact ionization of the supersonic beam and subsequent imaging of the produced CO$^+$ ions. We obtain an average neutral beam velocity of 870 m/s. For the translational temperature an upper limit of 70 K is estimated given the broadening of the velocity spread due to the momentum transfer from the impinging high energy electrons.

The ionic reaction products are extracted upward by pulsing the field plates of a velocity map imaging spectrometer. The detection scheme consists of a microchannel plate (MCP) attached to a phosphor screen. The impact position and arrival time are recorded by a CCD camera and a photomultiplier, respectively. The resulting laboratory image is transformed into a three-dimensional velocity vector in the center-of-mass frame. Each image presented in the upper row of Figure 1 consists of 4–5 × 10$^5$ product events. From the resulting center-of-mass product velocities the initial energy $E_{\text{int}}$ can be derived as the difference between the initially available energy, given by the collision energy $E_{\text{coll}}$ and the reaction exothermicity (denoted in reactions 1 and 2), and the final relative energy of the products, i.e., $E_{\text{int}} = (E_{\text{coll}} - \Delta H) - E_{\text{int}}^{\text{r}}$. In order to investigate the relative product isomer abundance, these distributions are fitted considering both the formation of one single (HCO$^+$) or two product species. The distribution is fitted with a function derived from a Gaussian velocity distribution:

$$p(E_{\text{int}}) = A \cdot \frac{\exp\left(\frac{-(E_{\text{max}} - E_{\text{int}})^2}{2\sigma^2}\right)}{\sqrt{E_{\text{max}} - E_{\text{int}}}}$$

where $E_{\text{max}}$ is the kinematical cutoff energy and corresponds to $E_{\text{max}} = (E_{\text{coll}} - (-1.76 \text{ eV}))$ for HCO$^+$ formation and $(E_{\text{int}} = (-0.13 \text{ eV}))$ for HOC$^+$ formation. The fit function depends on three parameters, namely, the amplitude $A$, the width $\sigma$, and the mean internal energy $E_{\text{int}}$. If only a one-isomer fit is considered, these parameters are optimized by a least-squares fit. In order to perform a two-component fit to the distribution both $\sigma$ and the relative energy loss are assumed to be equivalent for both isomer formations, i.e., $<E_{\text{HCO}}^{\text{r}}>/<E_{\text{HOC}}^{\text{r}}> = <E_{\text{HCO}}^{\text{T}}>/<E_{\text{HOC}}^{\text{T}}>$. The sum of both probability density functions produces the total two-component fit function, where only the two amplitudes remain as free parameters. These are optimized again by a least-squares fit and yield the isomer fractions.

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