







On the Energetics of the $\text{HCO}^+ + \text{C} \rightarrow \text{CH}^+ + \text{CO}$ Reaction and Some Astrochemical Implications

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Abstract

We explore the energetics of the titular reaction, which current astrochemical databases consider to be open at typical dense molecular (i.e., dark) cloud conditions. As is common for reactions involving the transfer of light particles, we assume that there are no intersystem crossings of the potential energy surfaces involved. In the absence of any such crossings, we find that this reaction is endoergic and will be suppressed at dark cloud temperatures. Updating accordingly a generic astrochemical model for dark clouds changes the predicted gas-phase abundances of 224 species by greater than a factor of 2. Of these species, 43 have been observed in the interstellar medium. Our findings demonstrate the astrochemical importance of determining the role of intersystem crossings, if any, in the titular reaction.

Key words: astrobiology – astrochemistry – ISM: molecules – molecular data – molecular processes

1. Introduction

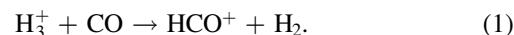
The chemistry of molecular clouds involves a complicated interplay of gas-phase reactions, chemistry on bare dust-grain surfaces, and processes on and in the icy mantles of grains (Herbst 2014; van Dishoeck 2014). Accurate chemical data are necessary for each of these domains. Experimental and theoretical work can provide rate coefficients for gas-phase chemistry. The situation is more challenging for grain-surface or ice chemistry, where the greater complexity and number of unknowns limit our ability to generate the needed rate coefficient data. Hence, it is critical to understand gas-phase reactions, in part so as to determine the importance and extent of grain-surface and ice chemistry. By comparing abundances from gas-phase astrochemical models to observations, one can determine whether or not the inferred abundance for a given molecule can be explained solely by gas-phase chemistry; if not, then that implies that either dust or ices are important, or that the gas-phase chemical data are inaccurate.

The gas-phase chemistry of clouds in the cold interstellar medium (ISM) is simplified by their typical densities and temperatures (Snow & McCall 2006; Herbst & Millar 2008). Due to the low densities, $\sim 10^3\text{--}10^7\text{ cm}^{-3}$, only two-body processes are important. The low temperatures, $\sim 10\text{--}100\text{ K}$, rule out many neutral-neutral chemical reactions as they generally possess significant activation energies. Hence, ion-neutral reactions (which typically possess no activation barrier) are extremely important; almost two-thirds of all reactions in current gas-phase astrochemical models are ion-neutral reactions (e.g., McElroy et al. 2013; Wakelam et al. 2015).

In dark clouds, gas-phase chemistry is initiated by cosmic-ray ionization of H_2 (Herbst & Klemperer 1973; Watson 1973). Nearly all of the resulting H_2^+ goes on to react exoergically with another H_2 molecule. This occurs on a timescale that is quite rapid compared to the lifetime of a molecular cloud. The resulting H_3^+ drives much of the ion-neutral chemistry in the cloud. Photoionization of H_2 is unimportant as ultraviolet and soft X-rays are strongly attenuated by the H and H_2 in the outer layers of the cloud; additionally, the photoionization

cross-sections due to hard X-rays and γ -rays are sufficiently small so as to minimize their contribution (Oka 2013).

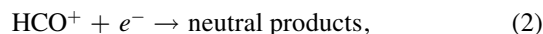
H_3^+ can then readily react with CO, the second most abundant neutral molecule in dark clouds (Garrod et al. 2007), via



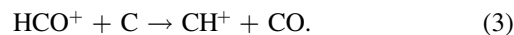
For “typical” dark cloud conditions (defined below), this reaction is important for cloud ages $\gtrsim 10^5$ years. The resulting HCO^+ is the most abundant molecular ion in dark clouds (Agúndez & Wakelam 2013). It has been detected in many such clouds, including TMC-1(CP) and L134N, which have estimated ages of $\sim 10^5$ years (Garrod et al. 2007).

The role of HCO^+ in the ISM has recently been briefly reviewed by Hamberg et al. (2014). The ion readily transfers its proton to many neutral molecules, thereby affecting the chemistry of molecular clouds. HCO^+ is also the dominant carrier of positive charge in dark clouds and is used to probe the degree of ionization of the cloud (Agúndez & Wakelam 2013). This is important as the dynamics of the cloud are modified by the presence of charge, which can couple to any ambient magnetic field, affecting the transfer of angular momentum and the dissipation of turbulence (Dalgarno 2006). The strength of this coupling is determined by the fractional ionization of the cloud. Hence, our knowledge of dark clouds and their evolution hinges, in part, on an accurate understanding of the underlying chemistry controlling the HCO^+ abundance.

To that end, we have investigated the gas-phase astrochemistry of HCO^+ using the Nahoon code (Wakelam et al. 2012) combined with the KInetic Database for Astrochemistry (KIDA; Wakelam et al. 2015). Our initial studies indicated that for dark cloud ages of $\sim 10^5$ years, the two most important HCO^+ destruction mechanisms are dissociative recombination (DR) with electrons via



and the ion-neutral reaction with atomic C



Reaction (2), DR of HCO^+ , has been extensively studied both theoretically and experimentally (for a review see Hamberg et al. 2014). Though some issues remain, it is thought to be relatively well understood. The same cannot be said for Reaction (3), for which there appears to be no theoretical or experimental studies. Present-day astrochemical models use the recommended rate coefficient of Prasad & Huntress (1980), which seems to be an estimate based on the Langevin formalism.

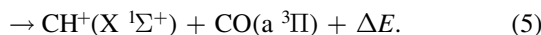
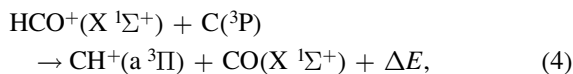
Given the apparent importance of Reaction (3), we explored the possibility of measuring it in our laboratory. Recently we have developed a novel dual-source, merged-beams apparatus for studying ion-neutral reactions. With this device we have measured reactions of H_3^+ with atomic C and O (O'Connor et al. 2015; de Ruelle et al. 2016) and investigated the astrochemical implications of our new chemical data (de Ruelle et al. 2016; Vissapragada et al. 2016). So it seemed a natural extension of that work to study Reaction (3). However, as we investigated the energetics of this reaction, we quickly realized that it was unlikely to be exoergic; rather, it is more likely to be endoergic by an amount sufficiently large for this channel to be closed at molecular cloud temperatures. This raises the question: what are the astrochemical implications of Reaction (3) being endoergic?

In the rest of this paper we explore these implications. Section 2 reviews the energetics of Reaction (3). Section 3 briefly discusses our dark cloud astrochemical model. Section 4 presents the results of our modeling and discusses some of the astrochemical implications of Reaction (3) being closed at dark cloud temperatures. Lastly, Section 5 summarizes our findings.

2. Energetics

In the cold ISM, molecules reside primarily in their lowest electronic state (X) and lowest vibrational level. The rotational populations are more sensitive to the temperature and density of the gas, but the bulk of the population typically resides in the lowest rotational levels. Rotational excitations have a negligible effect on the energetics of Reaction (3). For our calculations here, we assume that all parent and daughter molecules are in their lowest electronic, vibrational, and rotational levels.

The neutral C in dark clouds is of ^3P symmetry. The HCO^+ has a $^1\Sigma^+$ symmetry. Taking into account spin multiplicities (Talbi et al. 1991) and making the common assumption for reactions involving the transfer of light particles that intersystem crossings of the potential energy surfaces do not lead to substantial redistribution of the flux among the different spin symmetries (Salem & Rowland 1972; Li & Guo 2014; Martinez et al. 2015), the two lowest energy channels for Reaction (3) at 0 K are



Here ΔE is the reaction energy, defined here as the change in the total internal energies of the reactants and daughter products. ΔE is negative for endoergic reactions and positive for exoergic reactions.

The energies needed to calculate the energetics for Reactions (4) and (5) are given in Table 1. The dissociation

Table 1
Quantities Needed to Determine the Energetics for Reactions (4)–(6)

Process	D_e (eV)	ZPE (eV)	D_0 (eV)	$ \Delta E $ (eV)
$\text{HCO}^+(\text{X}^1\Sigma^+) \rightarrow \text{H}^+(\text{S}) + \text{CO}(\text{X}^1\Sigma^+)$	6.400	0.437	5.963	...
$\text{CH}^+(\text{X}^1\Sigma^+) \rightarrow \text{C}^+(\text{P}) + \text{H}(\text{S})$	4.264	...	4.085	...
$\text{CH}^+(\text{a}^3\Pi) \rightarrow \text{C}^+(\text{P}) + \text{H}(\text{S})$	3.068	0.167	2.901	...
$\text{CO}(\text{X}^1\Sigma^+) \rightarrow \text{C}(\text{P}) + \text{O}(\text{P})$	11.224	0.134	11.090	...
$\text{CO}(\text{a}^3\Pi) \rightarrow \text{C}(\text{P}) + \text{O}(\text{P})$	5.188	0.109	5.079	...
$\text{CO}(\text{X}^1\Sigma^+) \rightarrow \text{CO}(\text{a}^3\Pi)$	6.011
$\text{C}^+(\text{P}) + \text{H}(\text{S}) \rightarrow \text{C}(\text{P}) + \text{H}^+(\text{S})$	2.338

Note. D_e is the dissociation energy from the molecular potential minimum, ZPE is the zero-point energy of the lowest ro-vibrational level of the molecule, D_0 is the dissociation energy from this lowest level, and ΔE is the reaction energy. The various energies are taken from Huber & Herzberg (1976), Mladenović & Schmatz (1998), Barinovs & van Hemert (2004), Hechtfisher et al. (2002), Irikura (2007), Shi et al. (2013), Mladenović & Roueff (2014), Kramida et al. (2015), and M. Delsaut & J. Liévin (2017, in preparation).

energy from the molecular potential minimum is D_e . For HCO^+ , we take the value from Mladenović & Schmatz (1998) for the case where the H^+ is bound to the C. For CH^+ , we use the data of Barinovs & van Hemert (2004) and for CO that of Shi et al. (2013). For the reaction energetics, the quantity needed is the dissociation energy from the lowest ro-vibrational level, D_0 , which is D_e minus the zero-point energy (ZPE). Hechtfisher et al. (2002) measured D_0 for $\text{CH}^+(\text{X}^1\Sigma^+)$. We calculate D_0 for the other systems using the ZPE for HCO^+ from Mladenović & Roueff (2014), for $\text{CH}^+(\text{a}^3\Pi)$ from M. Delsaut & J. Liévin (2017, in preparation), and for $\text{CO}(\text{X}^1\Sigma^+)$ from Irikura (2007). For $\text{CO}(\text{a}^3\Pi)$, we have calculated the ZPE using the molecular constants of Huber & Herzberg (1976). We also note that the CH^+ D_0 is for dissociation to $\text{C}^+(\text{P}) + \text{H}(\text{S})$. Reactions (4) and (5) involve $\text{H}^+(\text{S})$ bonding to the $\text{C}(\text{P})$. Using the energies from Kramida et al. (2015), these lie an additional 2.338 eV above the products of the CH^+ dissociation limit.

From the information above, we can readily calculate ΔE for Reactions (4) and (5). For Reaction (4) we lose energy dissociating $\text{HCO}^+(\text{X}^1\Sigma^+)$ and gain energy going from $\text{C}(\text{P}) + \text{H}(\text{S})$ to $\text{CH}^+(\text{a}^3\Pi)$. This gives $\Delta E = -5.963 \text{ eV} + 2.901 \text{ eV} + 2.338 \text{ eV} = -0.724 \text{ eV}$, where the negative energy means that the reaction is endoergic. In a more chemical notation, the enthalpy of the reaction at 0 K is $\Delta_r H_0 = 69.9 \text{ kJ mol}^{-1}$, where a positive enthalpy signifies that the reaction is endoergic. The calculations are similar for Reaction (5), except that now we gain energy forming $\text{CH}^+(\text{X}^1\Sigma^+)$ and lose energy exciting the CO to the $\text{a}^3\Pi$ symmetry. This gives $\Delta E = -5.963 \text{ eV} + 4.086 \text{ eV} + 2.338 \text{ eV} - 6.011 \text{ eV} = -5.550 \text{ eV}$. The corresponding enthalpy of the reaction at 0 K is $\Delta_r H_0 = 535.4 \text{ kJ mol}^{-1}$, hence both reactions are endoergic by an amount $\Delta E/k_B = -8,402 \text{ K}$ for Reaction (4) and $-64,405 \text{ K}$ for Reaction (5), where k_B is the Boltzmann constant. All of these quantities have been calculated for 0 K. The energetics at dark cloud temperatures of $\sim 10 \text{ K}$ are essentially the same.

From this analysis, it is not clear why Prasad & Huntress (1980) treated Reaction (3) as being open with a thermal rate coefficient of $1.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In their compilation of reactions for gas-phase chemistry in interstellar clouds, they did not discuss the issues of spin multiplicities or intersystem crossings. It seems likely that they did not consider these

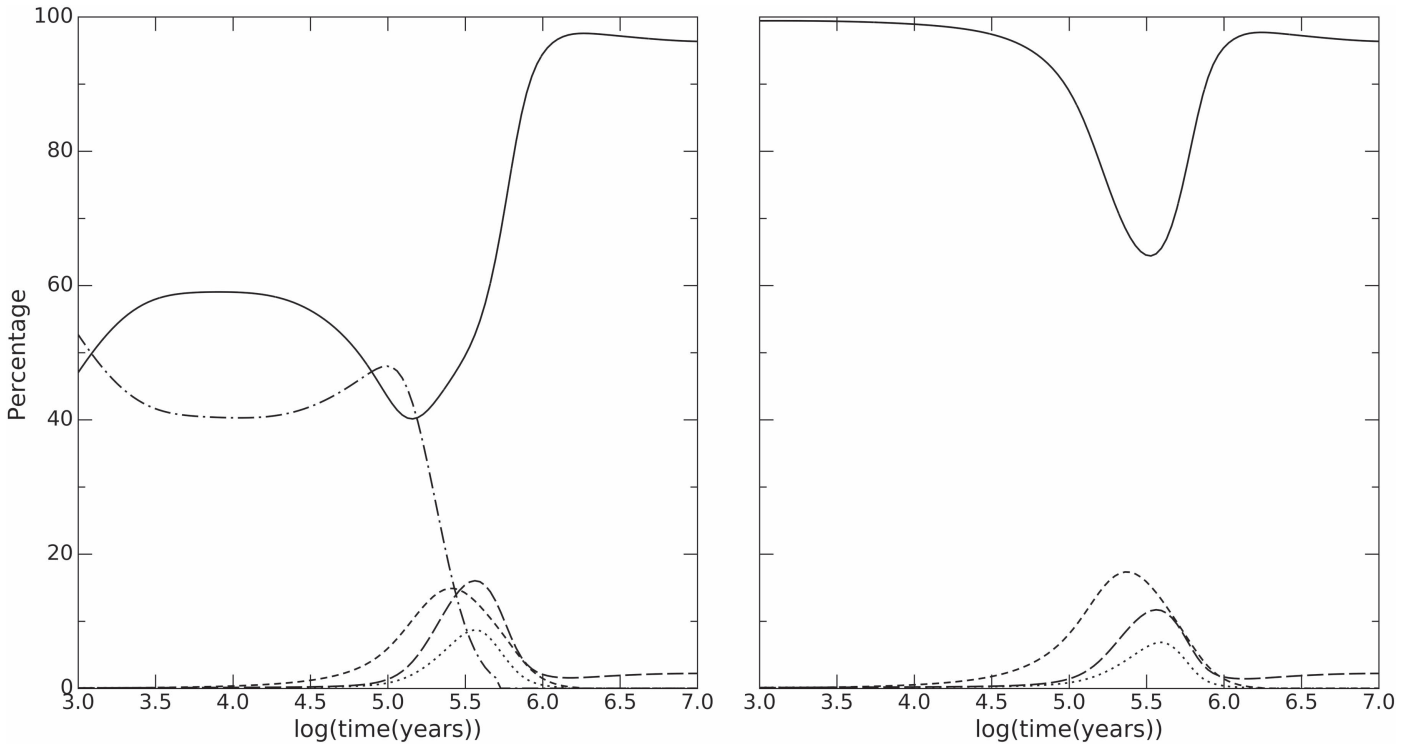
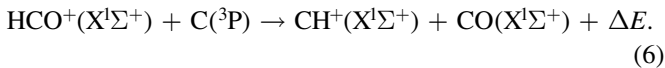


Figure 1. Most important HCO^+ destruction mechanisms, in percentage, for a generic dark cloud as a function of cloud age. The left panel shows the destruction mechanisms when Reaction (3) is treated as open, and the right panel when the reaction is closed. The solid curve is for DR (Reaction 2), the dotted–dashed curve is for the reaction with atomic C (Reaction 3), the short-dashed curve is for Reaction (11), the long-dashed curve is for Reaction (12), and the dotted curve is for Reaction (13).

issues, but rather just assumed that the CH^+ and CO both formed in their ground symmetries, namely



Here, the reaction would be exoergic by $\Delta E = -5.963 \text{ eV} + 4.085 \text{ eV} + 2.338 \text{ eV} = 0.460 \text{ eV}$ or $\Delta E/k_B = 5,338 \text{ K}$. The enthalpy would be $\Delta_r H_0 = -44.4 \text{ kJ mol}^{-1}$, where the negative sign signifies that the reaction is exoergic. But this channel would be open only if an intersystem transition occurred during the reaction. For now we follow the common practice of assuming that intersystem crossings are not important for reactions involving the transfer of light particles. Thus, below we assume that Reaction (3) does not proceed in the cold ISM. Definitively resolving this issue will likely require detailed theoretical and experimental chemical studies.

Lastly, we note that the enthalpy for some of the above reactions can also be calculated using the Active Thermochemical Tables hosted at Argonne National Laboratory.³ These tables do not provide the data needed for Reaction (4); however, they do give $\Delta_r H_0$ for Reactions (5) and (6) as $546.13 \pm 0.10 \text{ kJ mol}^{-1}$ and $-33.25 \pm 0.01 \text{ kJ mol}^{-1}$, respectively. These are about 11 kJ mol^{-1} larger than our values derived here, but do not change any of our conclusions about the energetics.

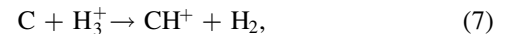
3. Dark Cloud Model

We adopt here the generic dark cloud conditions given by Wakelam et al. (2015), using their initial chemical abundances,

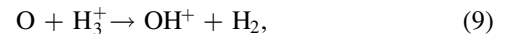
³ <http://atct.anl.gov/>

a visual extinction of $A_v = 30$, a hydrogen nuclei number density of $n_{\text{H}} = 10^4 \text{ cm}^{-3}$, a temperature of 10 K, and a cosmic-ray ionization rate for H_2 of $\zeta = 10^{-17} \text{ s}^{-1}$. The chemical evolution of the cloud is calculated using Nahoon (Wakelam et al. 2012) and a version of KIDA (Wakelam et al. 2015) which we have updated as described below. KIDA includes 489 species and over 7500 reactions.

We have modified KIDA slightly by incorporating our experimentally derived thermal rate coefficient results from O’Connor et al. (2015) for the reactions



Additionally, we use our experimental results from de Ruette et al. (2016) for



However, in this case we only extracted the thermal rate coefficient for the sum of both channels. Here we have assumed branching ratios of 100%:0% and 0%:100% for forming $\text{OH}^+:\text{H}_2\text{O}^+$, and find no difference in the results of our astrochemical simulations. We attribute this to OH^+ and H_2O^+ both undergoing rapid sequential hydrogen abstraction with the abundant H_2 to form H_3O^+ .

4. Astrochemical Implications

Figure 1 shows the dominant HCO^+ destruction mechanisms for our generic dark cloud as a function of the cloud age. The left panel shows the destruction mechanisms when

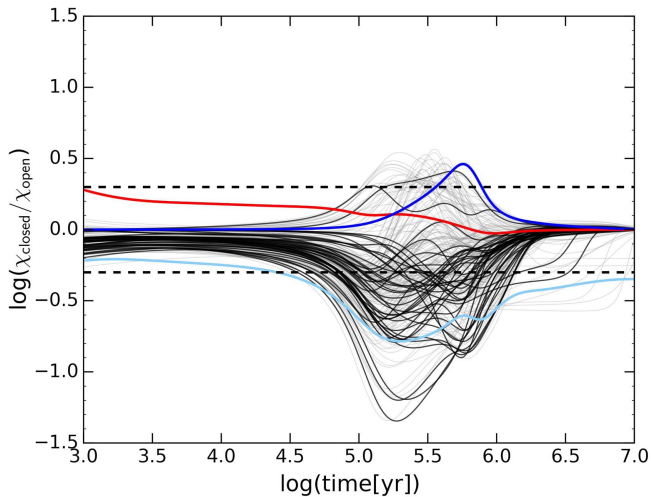
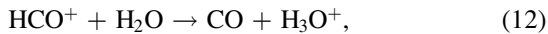
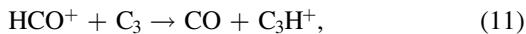


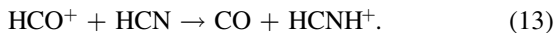
Figure 2. Ratios of the predicted abundances for all species in KIDA that are significantly impacted by the closing of Reaction (3) for cloud ages between 10^5 and 10^6 years. Abundances were calculated for the channel being closed (χ_{closed}) and assuming that the channel is open (χ_{open}). The log of the ratio is plotted as a function of cloud age for the initial conditions discussed in the text. The dashed lines represent the thresholds for “significantly” affected species (those with abundances that change by a factor of 2 or more). The red curve shows the abundance ratio for HCO^+ , the dark blue for C, and the light blue for CH^+ . The remaining gray and black curves are for all of the 222 other significantly affected species in KIDA, with the black curves showing the 43 of these that have been observed in the ISM.

Reaction (3) is treated as open and the right panel when the reaction is closed. If the reaction were indeed open, then the two dominant destruction mechanisms would be Reactions (2) and (3), with Reaction (3) becoming unimportant after $10^{5.3}$ years as the free atomic C becomes bound up into molecules. However, our energetics study indicates that Reaction (3) is closed, and that DR is the dominant HCO^+ destruction mechanism for all cloud ages.

In either case, for cloud ages between $\sim 10^5$ and 10^6 years, HCO^+ can also be destroyed via the minor reactions



and



The percentage contribution of these reactions to the total HCO^+ destruction rate are also shown in Figure 1.

We have also calculated the predicted abundances for all 489 species in KIDA. The abundances were calculated with Reaction (3) closed (χ_{closed}) and open (χ_{open}). The latter is currently assumed by astrochemical databases. Figure 2 shows the log of the relative abundance ratios $\chi_{\text{closed}}/\chi_{\text{open}}$, where we plot only those species with abundance ratios that change by a factor of 2 or more for cloud ages between 10^5 and 10^6 years. Also plotted for reference is the abundance ratio for HCO^+ .

The structure seen in Figure 2 can readily be explained by the changes in the abundances of CH^+ , C, and HCO^+ . The abundance of CH^+ is reduced by the closing of Reaction (3). As a result, the predicted abundances increase for those species which are destroyed by reactions with CH^+ . Closing Reaction (3) also generally increases the abundances of C and HCO^+ ; and the predicted abundances increase for those species

that are formed through reactions involving C and/or HCO^+ . Conversely, the abundances decrease for those species requiring CH^+ to form and/or if the precursors to these species are destroyed in reactions with C and/or HCO^+ .

For typical observed cloud ages of between 10^5 and 10^6 years, we find that the predicted abundances of 224 species change by more than a factor of 2. Of these species, 43 have been observed in the ISM. Many of these are predicted to form in the gas phase (Walsh et al. 2009; Agúndez & Wakelam 2013), such as the neutral hydrocarbons CH_3 , CH_4 , C_2H_2 , C_2H_4 , and CH_3CCH ; the amines CH_2NH_2 and CH_3NH_2 ; the cyanides and isocyanides HNC , CH_3CN , H_2CCN , and HNC_3 ; the polyynes and methylpolyynes C_4H_2 , $\text{CH}_3\text{C}_4\text{H}$, and $\text{CH}_3\text{C}_6\text{H}$; the cyanopolyynes HC_4N , HC_5N , and $\text{CH}_3\text{C}_3\text{N}$; and the molecular cations CH^+ , HCNH^+ , H_2COH^+ , and HC_3NH^+ .





5. Summary

HCO^+ is an important ion in the chemical and physical evolution of dark molecular clouds. We have explored the energetics of Reaction (3), which has long been assumed to be exoergic (Prasad & Huntress 1980) and as a result also appeared to be astrochemically important. However, in reactions involving the transfer of light particles it is commonly assumed that intersystem crossings are unimportant. If that is the case, then our results indicate that Reaction (3) is endoergic and will not proceed at typical molecular cloud temperatures. Our modeling of a generic dark cloud with this channel closed indicates that DR is the dominant destruction mechanism of HCO^+ at all cloud ages. We also find that the predicted abundances of 224 species change by greater than a factor of 2 as a result of closing Reaction (3). Our findings demonstrate the astrochemical importance of determining the role of intersystem crossings in Reaction (3).

As a final point, our findings are unlikely to have any impact on the long-standing issue of HCO^+ and CH^+ abundances in diffuse clouds (Godard et al. 2010; Valdivia et al. 2017). The observed abundances are 1 to 2 orders of magnitude larger than predicted by UV-dominated chemical models that include Reaction (3). If this reaction were closed, it would reduce the HCO^+ destruction rate, thereby increasing the predicted abundance. However, this is unlikely to result in an increase that is more than a factor of a couple, as DR is more likely to be the dominant HCO^+ destruction mechanism in either case. As for CH^+ , if Reaction (3) were closed, it would decrease the predicted CH^+ abundance, thereby further increasing the existing discrepancy between observations and models.

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