

# GRAIN SURFACE RECOMBINATION OF $\text{HCO}^+$

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## ABSTRACT

We investigate the recombination of the  $\text{HCO}^+$  ion on grain surfaces. This process is a key reaction in dense regions such as protoplanetary disks. The branching fraction among intact desorption, dissociation, and desorption with dissociation has been analyzed by a classical trajectory approach. It is found that dissociation (with or without desorption) dominates over intact desorption.

*Subject headings:* dust, extinction — ISM: molecules — molecular processes

## 1. INTRODUCTION

The theoretical study of molecular evolution in protoplanetary disks has shown that a significant fraction of the recombination between positive molecular ions and electrons occurs on grain surfaces, while it occurs in the gas phase in interstellar clouds (Aikawa et al. 1997, 1999). In a disk at radius  $R \gtrsim 10$  AU, most of the grains are negatively charged (Umebayashi & Nakano 1988). Because of the high density within the disk ( $n_{\text{H}} \gtrsim 10^8 \text{ cm}^{-3}$ ), the electron abundance is much lower and the collision timescale of an ion with a grain particle is much shorter than in interstellar clouds. Recombination of simple molecular ions in the gas phase is dissociative because radiative stabilization of the parent neutral is inefficient (Bettens & Herbst 1995). For example,  $\text{HCO}^+$  recombines to form CO and H (Tomashevsky, Herbst, & Kraemer 1998; Butler, Babcock, & Adams 1997). In the case of grain-surface recombination, on the other hand, it is not clear whether the reaction is dissociative. Some fraction of the parent neutral product (e.g., HCO) might be stabilized by depositing the excess energy onto the grain. In their investigation of molecular evolution in the outer regions ( $R \gtrsim 10$  AU) of the protoplanetary disks, Aikawa et al. (1997, 1999) found that the grain-surface recombination of  $\text{HCO}^+$  plays a critical role in the disk chemistry. If it is nondissociative, most of the gas-phase CO is transformed into other molecules via HCO within the lifetime of the disk. Since CO has been frequently used for surveys of gaseous disks, consideration of its abundance is important for the interpretation of observational studies. Thus, it is useful to investigate whether the grain-surface recombination of  $\text{HCO}^+$  is dissociative or not.

To date, not much work has been done on this subject. In a related study, Bates & Herbst (1988, and references therein) considered the recombination of positive ions with negatively charged polycyclic aromatic hydrocarbons (PAHs) theoretically and concluded that it is difficult to predict to what extent the reaction is dissociative for a particular ion without performing detailed calculations.

To complicate matters, there are two possible processes when a molecular ion approaches a negatively charged grain. The grain-surface electron may tunnel to  $\text{HCO}^+$  before the ion hits the grain. In that case recombination

occurs in the gas phase, producing CO and H. Another possibility is that the recombination occurs on the grain surface. In this paper we treat the latter case. Although some fraction of the reaction may follow the former mechanism, our focus is reasonable considering the following two points. First,  $\text{HCO}^+$  and the electron have to be very close (within a few angstroms) for the electron to tunnel to the ion through the potential well of depth a few eV between the electron and the grain. Second, the timescale for the electron to scan a grain surface is significantly long. The timescale for the ion at a distance of a few angstroms to reach the grain surface with thermal speed ( $\sim 10^4 \text{ cm s}^{-1}$  at 10 K) is  $\sim 10^{-12}$  s, while the timescale for an electron to scan the surface of a typical interstellar grain (with radius  $\sim 10^{-5}$  cm) is of order  $10^{-9}$  s assuming the potential barrier between the adsorption sites to be  $\sim 0.5$  eV (Tielens & Allamandola 1987). Thus, at least a significant fraction of the recombination should occur on the grain surface following the collision of the ion with the grain. Since the detailed mechanism of recombination between an ion and an electron on a grain surface is not understood, we assume here that the energy of recombination is distributed randomly among the H, C, and O atoms immediately after recombination. This hypothesis was not made in our gas-phase calculation of  $\text{HCO}^+$  recombination (Tomashevsky et al. 1998), where, following the curve-crossing hypothesis, the initial energy was placed mainly into potential energy of the H–C bond, which immediately breaks. Because of the assumptions made here, our results give an upper limit to the branching fraction of nondissociative recombination.

In this paper we investigate the recombination of  $\text{HCO}^+$  on a grain surface by the classical trajectory approach. Our model for the system is described in § 2. The results of the numerical calculations and their implications for disk chemistry are discussed in § 3.

## 2. MODEL

The model adopted in this work is essentially the same as described in Dzegilenko, Uzer, & Herbst (1996). As shown in Figure 1, the system consists of a linear HCO molecule physically adsorbed atop a surface atom on a grain surface with a vertical geometry. We consider two possible arrange-

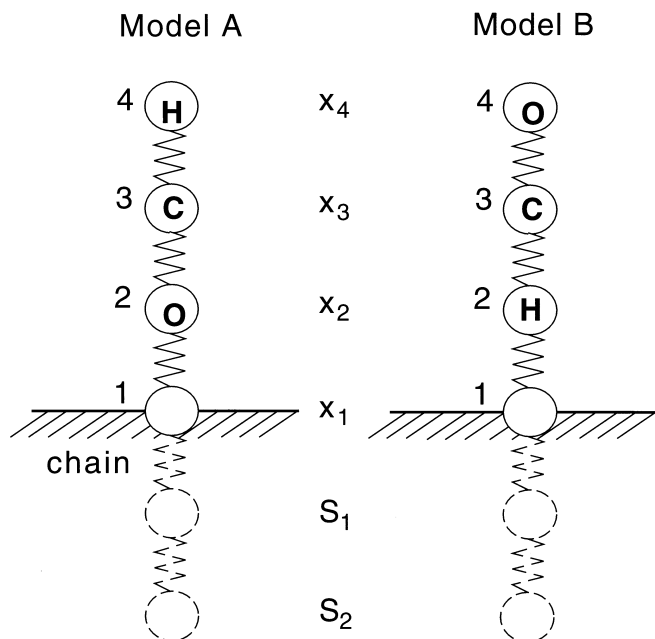


FIG. 1.—Schematic diagram of the adsorbed molecule system. The solid surface is approximated as a fictitious chain of atoms via the general Langevin model.

ments: model A, in which the HCO molecule is aligned so that the O atom is attached to the surface, and model B, in which the H atom is attached to the surface. In order to mimic a realistic interstellar grain, we assume the grain surface to be made of water ice. Our assumptions of a linear structure for HCO aligned perpendicularly to the surface are made for simplicity; in reality the free HCO molecule is bent with a bond angle of 119°6, and HCO may lie on the grain at various angles to the surface. Although we ignore these complications, we should still be able to estimate the efficiency of energy transfer from the recombined surface HCO molecule to the grain and thus be able to predict qualitatively, at least, whether the recombination is mainly dissociative or whether enough energy goes into the grain to prevent dissociation from occurring.

The total classical Hamiltonian for the HCO molecule plus an atom at the adsorption site is given in Cartesian coordinates by

$$H = \sum_{i=1}^4 \frac{p_i^2}{2m_i} + \sum_{i=1}^3 D_{i,i+1} \times \{1 - \exp[-\beta_{i,i+1}(x_{i+1} - x_i - x_{i,i+1}^{\text{eq}})]\}^2, \quad (1)$$

where  $i = 1$  refers to the surface site atom,  $i = 2, 3, 4$  refers to the atoms of the adsorbed HCO molecule in order of increasing distance  $x_i$  from the surface, the  $m_i$  represent the mass of each atom, and the  $p_i$  represent the conjugate momenta. A Morse oscillator-type potential is adopted both for the chemical bonds within HCO and for the physisorption bond between HCO and the surface site atom. For each bond between  $i$  and  $i + 1$ ,  $D_{i,i+1}$  is the dissociation energy,  $x_{i,i+1}^{\text{eq}}$  is the equilibrium distance, and  $\beta_{i,i+1}$  is a parameter related to the harmonic force constant. The parameters of the potential and the atomic masses are given in Table 1. The parameters for the bonds within the HCO molecule are taken from Herzberg (1966). For the disso-

TABLE 1  
PARAMETERS FOR THE COUPLED MORSE  
POTENTIALS

Parameter	Value	Value
$x_{1,2}^{\text{eq}}$ (Å) .....	2.17	2.17
$x_{2,3}^{\text{eq}}$ (Å) .....	1.19	1.08
$x_{3,4}^{\text{eq}}$ (Å) .....	1.08	1.19
$D_{1,2}$ (cm <sup>-1</sup> ) .....	911.2	911.2
$D_{2,3}$ (cm <sup>-1</sup> ) .....	66415.0	4798.26
$D_{3,4}$ (cm <sup>-1</sup> ) .....	4798.26	66415.0
$\beta_{1,2}$ (Å) <sup>-1</sup> .....	1.40	1.40
$\beta_{2,3}$ (Å) <sup>-1</sup> .....	2.25	4.56
$\beta_{3,4}$ (Å) <sup>-1</sup> .....	4.56	2.25
$m_1$ (amu) .....	18.0	18.0
$m_2$ (amu) .....	16.0	1.00
$m_3$ (amu) .....	12.0	12.0
$m_4$ (amu) .....	1.00	16.0

ciation energy and the equilibrium distance of the HCO-solid physisorption bond, we refer to the study of CO adsorbed onto H<sub>2</sub>O ice by Allouche, Verlaque, & Pourcin (1998). Because of the lack of data, we assume  $\beta_{1,2} = 1.4$  Å<sup>-1</sup>, which is taken from studies of the CO-NaCl physisorption bond (Dzegilenko et al. 1996, and references therein). Changing the value of  $\beta_{1,2}$  does not affect our results significantly.

The lattice is described classically in terms of the “generalized Langevin” model (Adelman 1979) and is treated as a linear atomic chain composed of coordinates representing the surface atom and  $n$  ( $n = 10$  in our calculations) fictitious internal atoms. Each atom in the chain is coupled harmonically with its nearest neighbors. Although it is described by a small number of chain atoms, this model incorporates the effect of the solid as a heat bath in a formally exact manner through dissipative and stochastic forces. The classical equations of motion for the chain atoms are

$$\ddot{x}_1 = -\omega_{e0}^2 x_1 + \omega_{c1}^2 S_1 - \frac{\partial V_a}{\partial x_1} \frac{1}{m_1}, \quad (2)$$

$$\ddot{S}_1 = -\omega_{e1}^2 S_1 + \omega_{c1}^2 x_1 + \omega_{c2}^2 S_2, \quad (3)$$

$$\ddot{S}_2 = -\omega_{e2}^2 S_2 + \omega_{c2}^2 S_1 + \omega_{c3}^2 S_3, \quad (4)$$

$$\ddot{S}_n = -\Omega_n^2 S_n + \omega_{cn}^2 S_{n-1} - \beta_n \dot{S}_n + R_t, \quad (5)$$

where the  $S_i$  are the displacement coordinates of the chain atoms,  $V_a$  is the potential in the Hamiltonian of equation (1), the  $\omega_{en}$  and  $\omega_{cn}$  are reduced harmonic force constants, and the last two terms in equation (5) are dissipative and stochastic forces. The parameters  $\omega_{en}$ ,  $\omega_{cn}$ ,  $\Omega_n$ , and  $\beta_n$  were computed using the method of Adelman (1979) with the Debye model of the solid. We adopted the Debye frequency of water ice (133.4 cm<sup>-1</sup>) in our calculation. In order to check the dependence of the results on Debye frequency we also performed the calculation with a frequency of 444.8 cm<sup>-1</sup>, which corresponds to solid Si. Since we are interested in the recombination reaction in the outer, low-temperature region of a protoplanetary disk ( $T \lesssim 50$  K), the stochastic force  $R_t$  is neglected in our calculation.

Initial values for the separation coordinates  $r_i = x_{i+1} - x_i$  for each of three Morse oscillators are obtained from the well-known distribution function for the Morse

oscillator (Porter & Raff 1976), assuming that the system is in its ground vibrational state before the recombination. The phase of the motion of each atom is randomized. The excess energy  $E_{\text{ex}}$  generated by the recombination is randomly distributed among the three atoms in HCO as a kinetic energy. The value of the excess energy is somewhat uncertain because of the adsorption energy of an electron on the grain surface. In this paper we consider two limiting cases. First, we adopt  $E_{\text{ex}} = 65,269.8 \text{ cm}^{-1}$ , assuming that the adsorption energy of the electron is negligible and that the energy is just the Coulomb energy of recombination. Since the electron has an adsorption energy of order  $\approx 1 \text{ eV}$  ( $8 \times 10^3 \text{ cm}^{-1}$ ) in reality (e.g., Umebayashi & Nakano 1980), our estimate is an upper limit of the excess energy. We also consider the case in which the adsorption energy of the electron is  $4.85 \text{ eV}$  ( $39117.9 \text{ cm}^{-1}$ ), and thus the excess energy is  $E_{\text{ex}} = 26,151.9 \text{ cm}^{-1}$ . This adsorption energy corresponds to the work function of a neutral Si solid and pertains to recombination on a neutral portion of the surface. In other words, the molecular ion strikes the grain surface and recombines with a normal bound electron, which is the only possible mechanism for neutral grains. In the outer region of the protoplanetary disk, most of the grains are negatively charged, and the adsorption energy for the excess electron(s) is smaller than that for the neutral solid. Thus the excess energy adopted in the latter case is a lower limit.

For each parameter set of arrangements, excess energy, and Debye frequency, a total of 1056 trajectories were run with random numbers generating initial conditions. The classical equations of motion were integrated by using a third-order Beeman numerical integration method out to a total integration time of 12.5 ps. The first integration step was performed by the fourth-order Runge-Kutta method. The standard checks on trajectory accuracy—varying the time step, monitoring the total energy of the system without the dissipation force, and running trajectories backward from the final to the initial points and comparing with the initial values of coordinates and momenta—are performed, and the results are satisfactory. Energy conservation is obeyed to five significant figures.

### 3. RESULTS AND DISCUSSION

The outcomes of the trajectories can be divided into four classes. These are: both desorption and dissociation (D+D), dissociation (D), intact desorption (ID), and no

reaction other than recombination on the grain (NR). Trajectories with  $x_2 - x_1$  larger than  $10 \text{ \AA}$  at the end of the integration time were regarded as desorbing, while trajectories with a distance between H and C ( $x_4 - x_3$  in model A and  $x_3 - x_2$  in model B) larger than  $10 \text{ \AA}$  were regarded as dissociating. Since the dissociation energy of CO is larger than the excess energy obtained from the recombination plus the initial vibrational energy, the C=O bond cannot dissociate. Table 2 shows the number of trajectories leading to each trajectory class mentioned above. It can be seen that dissociative trajectories (D+D plus D) dominate in all parameter sets. The fraction of nondissociative trajectories (ID and NR) depends on the excess energy obtained from the recombination; the fraction is larger in the case of the small excess energy. Even with this value,  $2.6 \times 10^4 \text{ cm}^{-1}$ , which can be regarded as a lower limit (see § 2), the nondissociative branching fraction is  $\sim 8 \times 10^{-2}$ .

Of the two dominant classes of trajectory results, desorption and dissociation (D+D) and dissociation (D), the D+D class is by far the more probable except for the calculation with model B, a small excess energy, and a large Debye frequency. Thus, our results show that, for the most part, the products of HCO<sup>+</sup> recombining on grain surfaces are gas-phase H and CO species. This result mirrors both the gas-phase result and the result for recombination by tunneling of a surface electron onto the HCO<sup>+</sup> ion before it strikes the grain surface. For those trajectories that result in dissociation without total desorption, one fragment of the molecule desorbs, either H (model A) or CO (model B). Any H remaining on the surface will either react quickly or evaporate. Any CO remaining will either evaporate or be partially hydrogenated into formaldehyde and methanol. Evaporation dominates if the temperature is sufficiently higher than its sublimation temperature of about 20 K.

Figure 2 shows a histogram of the number of trajectories versus energy deposited onto the grain for the calculation with model A, an excess energy of  $65,269.8 \text{ cm}^{-1}$ , and a Debye frequency of  $133.4 \text{ cm}^{-1}$  (water ice). The histogram has a double-peaked shape. The efficiency of energy deposition is dependent on the phase of motion of the atoms, especially the phase of the atom that can contact the surface; if it is moving toward the surface initially, the energy transfer is rather efficient. Still, even for those trajectories that transfer large amounts of energy, dissociation is often the outcome. The average value of the deposited energy is  $8000.7 \text{ cm}^{-1}$ , which is much smaller than the

TABLE 2  
RESULTS OF TRAJECTORIES BY NUMBER AND AVERAGE ENERGY FRACTIONS

$E_{\text{ex}}$ ( $\text{cm}^{-1}$ )	Debye Frequency ( $\text{cm}^{-1}$ )	D+D	D	ID	NR	$f_{\text{dep}}$	$f_{\text{trans}}$	$f_{\text{local}}$
Model A								
65269.8.....	133.4	776	238	42	0	0.12	0.26	0.62
65269.8.....	444.8	824	190	42	0	0.10	0.28	0.62
26151.9.....	133.4	600	372	84	0	0.12	0.22	0.66
26151.9.....	444.8	680	292	84	0	0.09	0.25	0.66
Model B								
65269.8.....	133.4	854	158	44	0	0.22	0.47	0.31
65269.8.....	444.8	656	370	30	0	0.15	0.52	0.33
26151.9.....	133.4	694	282	80	0	0.14	0.50	0.36
26151.9.....	444.8	430	538	88	0	0.19	0.46	0.35

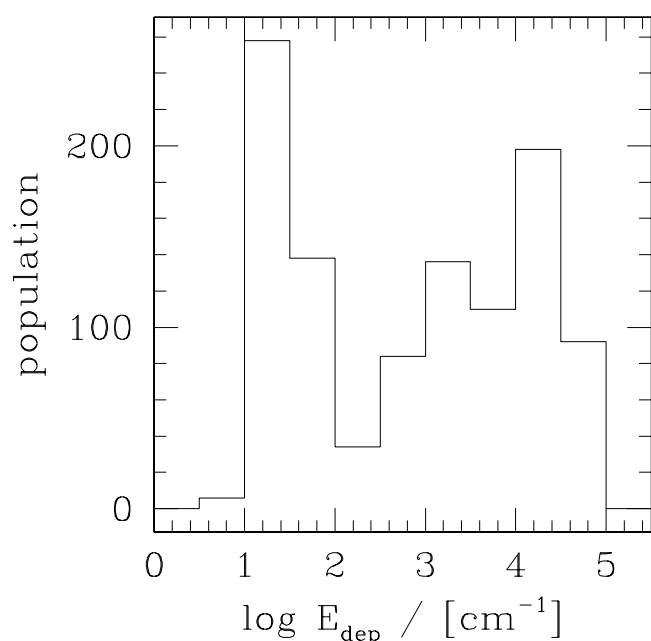


FIG. 2.—Histogram of the number of trajectories (population) vs. deposited energy ( $E_{\text{dep}}$ ) onto grains for model A, with an assumed excess energy of  $65,269.8 \text{ cm}^{-1}$  and a Debye frequency of  $133.4 \text{ cm}^{-1}$  (water ice).

excess energy of  $65,269.8 \text{ cm}^{-1}$  obtained from the recombination.

The right part of Table 2 shows the average fraction  $f$  of the total energy at the end of the calculation (12.5 ps) distributed among deposited energy onto the grain, translational energy of  $\text{HCO}$  as a whole, and local vibrational energy of  $\text{HCO}$ . The total energy is the recombination energy plus the ground-state vibrational energy ( $2.2 \times 10^3 \text{ cm}^{-1}$ ), which is given as an initial condition. The energy distribution is fixed after a few picoseconds in most of the trajectories. In the case of dissociation without desorption the energy distribution is not totally fixed; the translational energy changes in an oscillatory manner by 20%–30% after 3 ps. The final energy distribution mainly depends on the

geometry and does not depend much on either the Debye frequency or the excess energy. More energy is distributed to the local molecular vibrational modes in model A, in which the strong  $\text{C}=\text{O}$  bond is placed between two other bonds. In both model A and model B, only 10%–20% of total energy, on average, is deposited on the grain.

From the numerical calculations we have undertaken, we can safely conclude that, despite our simplifications, the grain-surface recombination of  $\text{HCO}^+$ , and probably all other small molecular ions, is mostly dissociative in nature. This conclusion leads to some important conclusions for the molecular evolution in protoplanetary disks. First, we can now expect that, contrary to our earlier conclusions (Aikawa et al. 1997), CO remains the most dominant form of carbon in the gas phase. The abundance of CO molecules remains almost constant [ $n(\text{CO})/n_{\text{H}} \sim 10^{-4}$ ] during the lifetime of the disk, which implies that CO is a good tracer of the gaseous component at least in the regions where the temperature is higher than its sublimation temperature ( $T \sim 20 \text{ K}$ ). A second point concerns deuterium chemistry in protoplanetary disks, which has been investigated recently by Aikawa & Herbst (1999). The products of the  $\text{HCO}^+$  and  $\text{DCO}^+$  recombination reactions on grain surfaces strongly affect the evolution of the DCN/HCN ratio in a disk. If the grain-surface recombination is nondissociative, DCN is formed through DCO, the product of the recombination reaction of  $\text{DCO}^+$ . Otherwise, DCN is formed more slowly through a chain of ion-molecule reactions starting from the precursor ion  $\text{CH}_2\text{D}^+$ . Aikawa & Herbst (1999) found that the assumption of dissociative recombination on grain surfaces better reproduces the DCN/HCN ratio observed in comet Hale-Bopp. Our result here is consistent with their argument.

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