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A COMBINED EXPERIMENTAL AND THEORETICAL STUDY OF THE REACTION OF DICARBON (C_2) WITH D1-ACETYLENE (HCCD): POSSIBLE MECHANISMS FOR DEUTERIUM ENRICHMENT IN THE INTERSTELLAR D1-BUTADIYNYL RADICAL, CCCCD($X^2\Sigma^+$)

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ABSTRACT

The reaction of the dicarbon molecule (C_2) with D1-acetylene (HCCD) was carried out under single-collision conditions in a crossed molecular beams machine to investigate deuterium enrichment processes in cold molecular clouds and in circumstellar envelopes of carbon stars. The experiments were merged with electronic structure calculations. Our combined experimental and theoretical studies suggest that this barrierless neutral-neutral reaction can induce a deuterium enrichment in the D1-1,3-butadiynyl radical (CCCCD) over a broad range of collision energies formally corresponding to temperatures from 10 to a few thousand kelvin as present in cold molecular clouds and circumstellar envelopes close to the photosphere, respectively. Generalized, each rapid, neutral-neutral reaction, which proceeds through indirect scattering dynamics via a reaction intermediate residing in a deep potential energy well, can induce a deuterium enrichment in cold molecular clouds (10 K) and even at elevated temperatures of a few thousand K as present, for instance, in the envelope of the dying carbon star IRC +10216. These findings should trigger an astronomical survey of the D1-1,3-butadiynyl molecule in the circumstellar shells of IRC +10216.

Subject headings: ISM: molecules — molecular processes

1. INTRODUCTION

The exploration of the deuterium fractionation in the interstellar medium presents an important means to examine chemical models on the evolution of cold molecular clouds and of carbon-rich circumstellar envelopes (Roberts et al. 2002, 2004; Osamura et al. 2005). Compared to the interstellar D/H abundances of about 10^{-5}, deuterium enrichments up to a factor of 10^3 can be observed in interstellar molecules (Sandford 2002; Herbst 2003; Millar 2003; Rodgers & Charnley 2002). So far, about 32 isotopomers have been detected ranging from mono- via di- to triply deuterated molecules. These are, for instance, the singly deuterated species D-thioformaldehyde (HDCS), D-ethynyl (CCD; Combes et al. 1985; Vrtilek et al. 1985), D-water (HDO; Walmsley et al. 1989), D-cyclopropenylidene (c-C_3HD; Bell et al. 1988), D-tricarbonhydride (C_3D; Turner 1989), D-ammonia (NH_2D; Millar & Brown 1989; Saito et al. 2000; Hatchell 2003), D-methanol (CH_2DOH; Parise et al. 2002; Millar & Brown 1989; Herbst 1992), D-formaldehyde (HDCO; Herbst 1992), D-hydrogencyanide (DCN; Irvine & Knacke 1989), D-iso hydrogencyanide (DNC), D-cyanoacetylene (DCCCN), D-cyanodiacetylene (DCCCCCN; Herbst 1992), D-methylacetylene (CH_2DCCH; Gerin et al. 1992), D-hydrogen sulfide (HDS; van Dishoek et al. 1995), D-hydrogen (HD; Henchman et al. 1988), together with ions H_2D^+, DCO^+, and $DN_2{}^+$. D2-formaldehyde (D_2CO; Ceccarelli et al. 2002), D2-methanol (CHD_2OH; Parise et al. 2002), D2-hydrogensulfide (D_2S; Vastel et al. 2003), D2-ammonia (ND_2H; Roberts et al. 2004), and D_2H^+ (Vastel et al. 2004) comprise doubly deuterated species observed (Roberts et al. 2004). The recent detection of triply deuterated molecules D3-ammonia (ND_3; van der Tak et al. 2002) and D3-methanol (CD_3OH; Parise et al. 2004) yielded important clues on the relative importance of gas phase versus grain-surface reactions and their role in the deuterium enrichment of interstellar molecules (Roberts et al. 2004; Osamura et al. 2005).

In the gas phase, it is generally accepted that the essential principle leading to a deuterium enrichment involves exoergic ion-neutral reactions under thermodynamical equilibrium that have no entrance barrier (Roberts et al. 2002; Roberts & Millar 2000). For instance, considering the exoergic reactions (1)–(3), the deuterated molecular ions are suggested to be destroyed very slowly in the reversed, endoergic reactions at temperatures less than 100 K. These ions can react subsequently via D^+ transfer with molecules such as water (H_2O), carbon monoxide (CO), and acetylene (HCCH); this propagates the isotope effect further. The resulting ions can then undergo dissociative recombination with electrons; this leads, for example, to the formation of D1-acetylene (HCCD) via dissociative recombination of an electron with the D1-vinyl cation ($C_2H_2D^+$):

$$H_3^+ + HD \leftrightarrow H_2D^+ + H_2, \qquad (1)$$

$$CH_3^+ + HD \leftrightarrow CH_2D^+ + H_2, \qquad (2)$$

$$C_2H_2^+ + HD \leftrightarrow C_2HD^+ + H_2. \qquad (3)$$

But despite elaborate ion-neutral models, the mechanism leading to a deuterium enrichment in complex organic, hydrogen-deficient molecules like c/l-C_3H_2 and C_3H is far from being resolved (Bell et al. 1988; Maluendes et al. 1993). For instance, the synthesis of c-C_3H_2 and c-C_3DH is suggested to involve an elusive $C_3H_2D^+$intermediate that fragments on dissociative recombination to c-C_3H_2/C_3HD and C_3D/C_3H. However, the D/H ratio of 0.1 as found toward the molecular cloud TMC-1 could not be reproduced with this ion-neutral scheme; only D/H ratios between 0.004 and 0.02 were obtained in chemical reaction models simulating the deuterium fractionation in TMC-1 (Roberts et al. 2002). An alternative pathway leading to a deuterium enrichment at low temperatures could implicate rapid and barrierless neutral-neutral reactions (Kaiser 2002). A recent theoretical study of the neutral-neutral reaction of carbon atoms in their C(^3P_j)

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ground state reacting with D1-acetylene (DCCH) suggested that the formation of the linear isotopomer, l-$C_3H(^2\Pi_{1/2})$, plus atomic deuterium is endoergic by 5.8 kJ mol^{-1}; on the other hand, the reaction to yield l-$C_3D(^2\Pi_{1/2})$ plus atomic hydrogen was found to be exoergic by 0.3 kJ mol^{-1} (Kaiser et al. 1999). Therefore, this process can support a deuterium enrichment in the l-$C_3D(^2\Pi_{1/2})$ isomer at low temperatures as prevailing in molecular clouds such as TMC-1.

The deuterium enrichment in even more complex organic radicals like D-1,3-butadiynyl (CCCCD) as observed by Turner (1989) has not been fully understood either. This is pretty surprising, since the corresponding 1,3-butadiynyl radical (CCCCH) in its $^2\Sigma^+$ electronic ground state has received considerable attention due to its potential significance as a precursor to polycyclic aromatic hydrocarbons (PAHs) and possibly to fullerenes in the interstellar medium (Millar et al. 1997; Doty & Leung 1998; Minh & van Dishoek 2000; Teyssier et al. 2004a, 2004b). Recent crossed molecular beams experiments of dicarbon molecules (C_2) in their electronic ground ($X^1\Sigma_g{}^+$) and first electronically excited states ($a^3\Pi_u$) with acetylene (HCCH) suggest that the 1,3-butadiynyl radical [CCCCH($X^2\Sigma^+$)] can be formed in an exoergic and barrierless reaction under single-collision conditions via a dicarbon versus atomic hydrogen exchange pathway through cyclic and acyclic C_4H_2 reaction intermediates (Kaiser et al. 2003; Gu et al. 2006b). On the singlet surface, the reaction was found to be indirect and involved a barrierless decomposition of a diacetylene intermediate s3 (HCCCCH) (Fig. 1); in the triplet manifold, the bimolecular collisions were found to be rather direct and involved structure t3 and an exit barrier to form the 1,3-butadiynyl radical via an atomic hydrogen loss. In this paper, we investigate to what extent the reaction of dicarbon molecules with D1-acetylene (DCCH) can lead to a deuterium enrichment in the 1,3-butadiynyl radical (reactions [4] and [5]). The experimental studies (§ 2) are contemplated with electronic structure and statistical calculations (§ 3).

$$C_2 + HCCD \rightarrow CCCCH + D \tag{4}$$

$$C_2 + HCCD \rightarrow CCCCD + H. \tag{5}$$

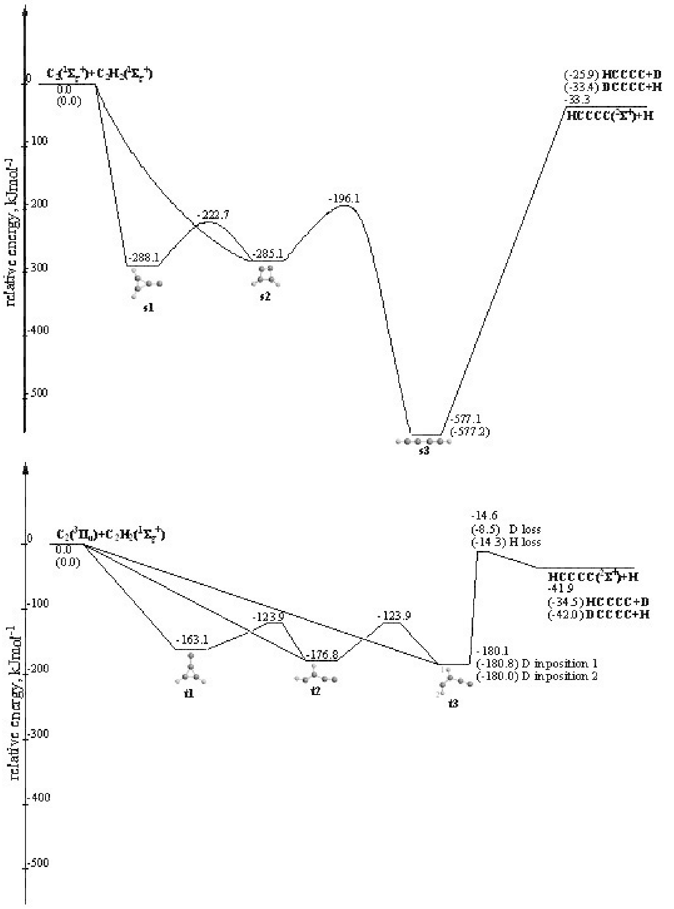

FIG. 1.—Simplified singlet and triplet potential energy surfaces of the reactions of dicarbon molecules with D1-acetylene; only pathways involved in the formation of 1,3-butadiynyl and D1-1,3-butadiynyl are shown; the numbers in parentheses correspond to the energetics of decomposing intermediates of the $C_2 + C_2HD$ reaction.

2. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

The experiments were conducted under single-collision conditions utilizing a universal crossed molecular beams setup (Gu et al. 2006a). Briefly, the main chamber consists of a stainless steel box and is evacuated to the low 10^{-8} torr region. The source regions, in which the pulsed supersonic beams of dicarbon (primary source) and D1-acetylene (secondary source) are generated, are located inside the main chamber. In the primary source, the 266 nm output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused on a rotating carbon rod. The ablated species [atomic carbon $C(^3P_j)$, dicarbon $C_2(X^1\Sigma_g{}^+/a^3\Pi_u)$, tricarbon $C_3(X^1\Sigma_g{}^+)$] were seeded in helium carrier gas released by a pulsed valve operated at 4 atm backing pressure (Gu et al. 2006a). A chopper wheel situated after the skimmer selected a part of the ablation beam that crossed the D1-acetylene beam perpendicularly in the interaction region; experiments were carried out at collision energies of $21.6 \pm 0.8, 29.0 \pm 0.6, 39.9 \pm 0.7,$ and 47.5 ± 1.2 kJ mol^{-1}. The reactively scattered products are monitored in the collision plane using a triply differentially pumped quadrupole mass spectrometer with a Brink-type electron-impact ionizer in the time-of-flight (TOF) mode, i.e., recording the time-dependent intensity of ions at distinct m/z-ratio at different laboratory scattering angles (Gu et al. 2006a). Note that although the beam contains tricarbon molecules, the latter were found not to interfere with the reactive scattering signal from the dicarbon reactions since bimolecular reactions of tricarbon with acetylene have a characteristic reaction threshold of about 85 kJ mol^{-1} (Kaiser et al. 2001); this value ranges well above the collision energy of our crossed beams experiments. For the physical interpretation of the reactive scattering data and for the determination of the branching ratios of reaction (4) versus reaction (5), it is crucial to transform the laboratory data into the center-of-mass (CM) system. Here information on the reaction dynamics is gained by fitting the TOF spectra and the laboratory angular distribution (LAB) using a forward-convolution routine (Vernon 1981; Weiss 1986; Kaiser et al. 1998). This iterative approach initially guesses the angular flux distribution $T(\theta)$ and the translational energy flux distribution $P(E_T)$ in the CM system, which are assumed to be independent of each other. Laboratory TOF spectra, laboratory angular distributions, and branching ratios of the hydrogen versus deuterium loss pathways (reactions [4] and [5]) are calculated then from these CM functions (Kaiser et al. 1998).

3. THEORETICAL PROCEDURE

The potential energy surfaces of the reactions of singlet and triplet dicarbon with acetylene have been published previously (Kaiser et al. 2003; Gu et al. 2006b). Here we expand these studies to the triplet and singlet D1-C_4HD surfaces. The geometries of various species were optimized at the density functional B3LYP/6-311G** level (Becke 1993; Lee et al. 1988). Vibrational frequencies calculated at this level were used for characterization of stationary points as minima and transition states, and for zero-point energy (ZPE) corrections. Single-point energies were then refined at the CCSD(T)/6-311+G(3*df*, 2*p*) level of theory (Purvis & Bartlett 1982). After the surfaces and molecular parameters were determined, statistical theories (Steinfeld et al. 1999) were utilized to compute product branching ratios. To compare our results with cross molecular beams experiments, we used microcanonical RRKM theory to calculate internal-energy-dependent rate constants for unimolecular steps. In microcanonical RRKM theory, rate constant $k(E)$ at internal energy E for a unimolecular reaction $A^* \rightarrow A^\# \rightarrow P$ is expressed as

$$k(E) = \frac{\sigma}{h} \frac{W^\#(E - E^\#)}{\rho(E)}, \qquad (6)$$

where σ is the reaction path degeneracy, h is Plank's constant, $W^\#(E - E^\#)$ denotes the total number of states for the transition state (activated complex) $A^\#$ with a barrier $E^\#$, $\rho(E)$ represents the density of states of the energized reactant molecule A^*, and P is the product or products. In the case of bimolecular reactions, the available internal energy E is the energy of chemical activation plus the collision energy. If no distinct transition state exists on the surface such as simple bond cleavages on the singlet surface from diacetylene to atomic hydrogen and the 1,3-butadiynyl radicals, we employed variational transition state theory (VTST; Steinfeld et al. 1999). Here different positions for the transition state along the reaction path were considered and partial geometry optimization of the transition state candidates with C-H (C-D) distances fixed at different values was carried out using the B3LYP/6-311G** method. Then $3N$–7 vibrational frequencies projected out of the gradient direction were calculated at the same theoretical level and the B3LYP/6-311G** relative energies of the optimized structures along the reaction path were scaled by a factor that matched the B3LYP/6-311G** and CCSD(T)/6-311+G(3*df*, 2*p*) relative energies of the final products of the H (D) loss. The variational transition states were finally determined by minimizing the RRKM-calculated rate constants for the H (D) loss reactions among all transition state candidates on the reaction path. The most detailed description of the ab initio/VTST/RRKM procedure to calculate microcanonical energy-dependent rate constants for barrierless reaction steps is given in a previous publication (Kislov et al. 2004). The GAUSSIAN 98 (Frisch et al. 1998) and MOLPRO 2002 ab initio program packages were utilized.

4. RESULTS

Reactive scattering signal was monitored at mass-to-charge ratios of $m/z = 50$ (C_4D^+; Fig. 2), $m/z = 49$ (C_4H^+; Fig. 2), and 48 (C_4^+). It should be stressed that the C_4D radical can only fragment via dissociative ionization to $m/z = 48$ (C_4^+), but not to $m/z = 49$ (C_4H^+); therefore, the experiments show explicitly that both the dicarbon versus deuterium (reaction [3]) and dicarbon versus hydrogen (reaction [4]) pathways are open. Similar to the crossed beams experiment of dicarbon with acetylene (Kaiser et al. 2003), we did not observe any molecular hydrogen elimination (here: HD elimination) to form tetracarbon molecules. Therefore, at all collision energies, signal at 48 (C_4^+) only originated from dissociative electron impact ionization of the neutral C_4D and C_4H radicals in the ionizer. We also integrated TOF spectra to provide the laboratory angular distributions (LAB) of the product isomer(s) at $m/z = 50$ (C_4D^+) and 49 (C_4H^+; Fig. 3). It should be stressed that at each angle and at each collision energy, the signal of C_4D^+ is systematically stronger than the signal of the corresponding C_4H^+ions. Also, due to the kinematics and hence the emission of the lighter hydrogen atom compared to the heavier deuterium atom, the LAB distribution of the C_4D product are narrower by about 5° compared to the C_4H laboratory angular distribution. It should be emphasized that within the error limits the TOF and LAB distributions could be fit with the same CM translational energy [$P(E_T)$] and angular [$T(\theta)$] functions as utilized in the fitting of the dicarbon plus acetylene reaction, for instance at a collision energy of 29.0 ± 0.5 kJ mol^{-1} as shown in Figure 4. Here the best fit of the TOF spectra and of the LAB distribution could be achieved with CM translational energy distributions from which a reaction exoergicity of 44 ± 5 kJ mol^{-1} could be derived. This compares reasonably well with the computed exoergicities of 25.9 and 33.4 kJ mol^{-1} (singlet surface; reactions [4] and [5]) and 34.5 and 42.0 kJ mol^{-1} (triplet surface; reactions [4] and [5]). We would like to stress again that the $T(\theta)$ values utilized to fit the experimental data are within the error limits identical to the one for the reaction of dicarbon with acetylene. This holds important consequences for the life time of the decomposing intermediate. Here the diacetylene molecule was inferred as the decomposing complex on the singlet C_4H_2 surface (Kaiser et al. 2003; Gu et al. 2006b; Fig. 1). However, the latter belongs to the $D_{\infty h}$ point group and holds an infinite number of C_2 rotation axes perpendicularly to the molecular axis; this would

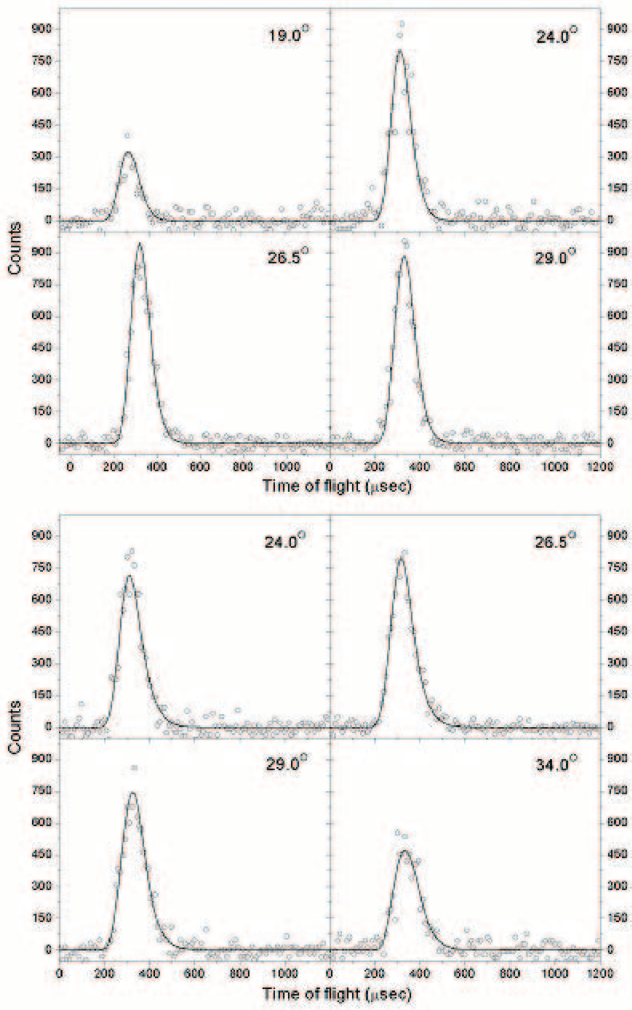

FIG. 2.—Selected time-of-flight data for $m/z = 50$ (C_4D^+) (*top*) and $m/z = 49$ (C_4H^+) (*bottom*) at a collision energy of 29.0 ± 0.6 kJ mol^{-1} depicting the flight time vs. the absolute ion counts. The circles indicate the experimental data, and the solid lines show the calculated fit.

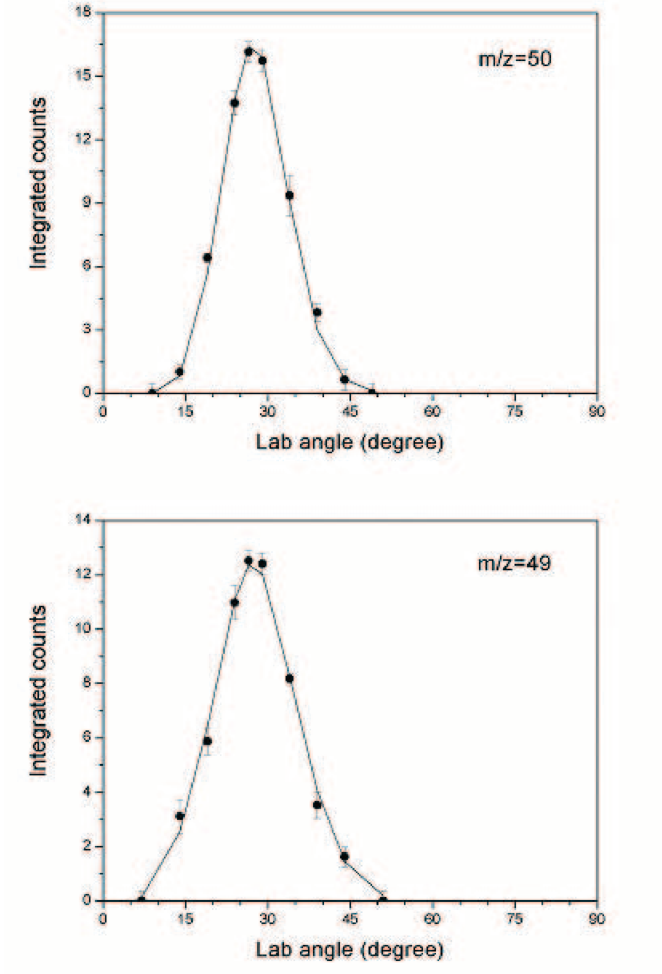

FIG. 3.—Laboratory angular distribution of the 1,3-butadiynyl radical recorded at $m/z = 50$ (C_4D^+) and $m/z = 49$ (C_4H^+) at a collision energy of 29.0 ± 0.6 kJ mol^{-1}. Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions. The direction of the dicarbon and D1-acetylene beams are defined as 0° and 90°, respectively.

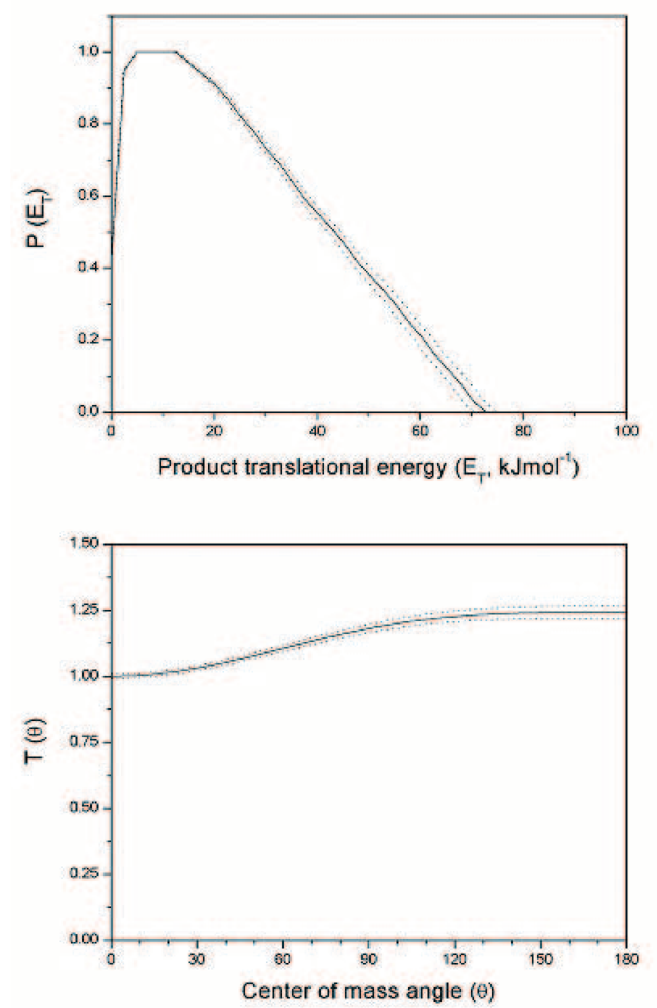

FIG. 4.—Translational energy (*top*) and center-of-mass angular flux distributions (*bottom*) for the reactions of dicarbon with D1-acetylene at a collision energy of 29.0 ± 0.6 kJ mol^{-1}. Solid lines are the best-fit functions, the dotted lines acceptable fits within the error limits.

yield a forward-backward symmetric CM angular distribution from the reaction on the singlet surface since both hydrogen atoms can be inter converted via a rotation around 180°, and the hydrogen atom can be emitted with equal probability into $\theta°$ and $\pi - \theta°$, even though the lifetime of the decomposing diacetylene molecule may be less than its rotational period. However, the reaction of dicarbon with D1-acetylene involves D1-diacetylene (HCCCCD) on the singlet surface. Here the incorporation of the deuterium atom reduces the symmetry to $C_{\infty v}$ and eliminates the C_2 rotation axes perpendicularly to the molecular axis.

These data can be employed now to calculate the branching ratios of reactions (5) versus (4) (Vernon 1981; Weiss 1986; Kaiser et al. 1998). Here we find branching ratios of 2.4 ± 0.3, 2.3 ± 0.3, 2.4 ± 0.3, and 2.6 ± 0.3 at collision energies of 21.6 ± 0.8, 29.0 ± 0.6, 39.9 ± 0.7, and 47.5 ± 1.2 kJ mol^{-1}, respectively. These branching ratios are computed from the ratio of the count rates of the signal at $m/z = 50$ versus $m/z = 49$ corrected for the mass factor of the reaction products (Schmoltner 1989); we also assumed that the transmission of $m/z = 50$ and 49 through the quadrupole system is identical—a reasonable assumption considering the mass difference of only 1 amu. Considering the branching ratios, about 70% of the C_4HD intermediates fragment via atomic hydrogen loss, whereas only 30% decompose via deuterium atom emission. It is important to compare these experimental findings with our theoretical calculations. Here we find that on the singlet surface, the unimolecular decomposition of D1-diacetylene (DCCCCH) leads also to a deuterium enrichment (Table 1). As the collision energies rise from 0 to 50 kJ mol^{-1}, the calculations suggest that the branching ratios of the hydrogen loss versus deuterium loss decrease only slightly from 2.3 to 2.0. On the triplet surface, we find ratios ranging from 5.8 to 2.2 at collision energies between 0 and 50 kJ mol^{-1}, respectively (Table 1). Therefore, even at collision energies of 50 kJ mol^{-1}, which corresponds formally to temperatures of about 6000 K, a deuterium enrichment in the 1,3-butadiynyl radical is evident. This—to our best knowledge—is the first combined experimental and theoretical evidence that deuterium enrichments are feasible at elevated temperatures up to a few thousand kelvin. The branching ratios of the hydrogen versus deuterium loss pathways—computed at the collision energies of 21.6, 29.0, 39.9, and 47.5 kJ mol^{-1}-on the singlet and triplet surfaces, agree well with our experimental values ranging within the error limits from 2.3 to 2.6. At present, we do not know the relative concentration of triplet versus singlet dicarbon in the beam. However, the computed branching

TABLE 1

Rate Constants and Branching Ratios

	Singlet (from s3)			Triplet (from t3)		
E_{col} (kJ mol^{-1})	k(D loss) (s^{-1})	k(H loss) (s^{-1})	k(H)/k(D)	k(D loss) (s^{-1})	k(H loss) (s^{-1})	k(H)/k(D)
0	3.55×10^6	8.06×10^6	2.268	1.11×10^7	6.49×10^7	5.833
10.6	8.06×10^6	1.76×10^7	2.179	1.02×10^8	3.75×10^8	3.682
12.1	8.99×10^6	1.95×10^7	2.168	1.31×10^8	4.61×10^8	3.532
21.6	1.72×10^7	3.62×10^7	2.112	4.96×10^8	1.44×10^9	2.898
29.0	2.73×10^7	5.66×10^7	2.076	1.14×10^9	2.99×10^9	2.617
39.9	5.10×10^7	1.04×10^8	2.034	3.15×10^9	7.43×10^9	2.356
47.5	7.62×10^7	1.53×10^8	2.011	5.70×10^9	1.28×10^{10}	2.235

Note.—Collision energy dependence of the rate constants and branching ratios involved in the atomic hydrogen and deuterium loss pathways on the singlet and triplet surfaces from s3 and t3, respectively.

ratios for the singlet and triplet surfaces are very similar and also in good agreement with our experimental values.

5. ASTROPHYSICAL IMPLICATIONS

Our combined experimental and theoretical investigations of the reaction of dicarbon molecules with D1-acetylene depicted explicitly that a deuterium fractionation can be achieved via a barrierless and exoergic reaction between two neutral particles to form D1-1,3-butadiynyl radicals, CCCCD($X^2\Sigma^+$), in the interstellar medium. This process could account for the hitherto unexplained column densities of D1-1,3-butadiynyl as observed in the cold molecular cloud TMC-1 (Turner 1989). We would like to recall that in cold molecular clouds, where typical temperatures of 10–20 K reside, dicarbon molecules exist solely in their $X^1\Sigma_g{}^+$ electronic ground state; however, at elevated temperatures of 3000 K as present close to the photosphere of the circumstellar envelope of the carbon-rich star IRC +216, a fraction up to 68% of the dicarbon molecules can also exist in their first electronically excited state, $a^3\Pi_u$. Secondly, our investigation verified that the branching ratio of the unimolecular decomposition of the singlet D1-diacetylene intermediates to form CCCCD($X^2\Sigma^+$) versus CCCCH($X^2\Sigma^+$) is almost constant over the temperature range from 0 to 6000 K. This means that even in the circumstellar envelope of IRC +10216, a deuterium fractionation can be sustained although temperatures can rise up to a few thousand kelvin. We would like to elucidate briefly on this finding. It should be recognized that the reaction of singlet dicarbon with D1-acetylene involves indirect scattering dynamic and hence the formation of reaction intermediates (Fig. 1). Here the D1-diacetylene intermediate s3 is stabilized by 577 kJ mol^{-1} with respect to the separated reactants. This means that—by computing the unimolecular decomposition of D1-diacetylene and hence the branching ratios of the hydrogen versus deuterium loss—the D1-diacetylene molecules has at least an internal (vibrational, rotational) energy of 577 kJ mol^{-1}. By increasing the collision energy from 0 kJ mol^{-1} (formally representing cold molecular clouds) to 50 kJ mol^{-1} (formally representing the high temperature regions close to the photosphere of carbon stars), the *total* internal energy available for a unimolecular decomposition of the D1-diacetylene molecule either via atomic hydrogen or deuterium loss increases to 627 kJ mol^{-1} by only about 9%. Therefore, we can conclude that the more the decomposing reaction intermediate is stabilized with respect to the separated reactants, i.e., the deeper the potential energy well of the intermediate is, the less influence the collision energy and hence the temperature of the interstellar environments has on the deuterium isotope fractionation. This versatile concept suggests that neutral-neutral reactions, which proceed via indirect reaction dynamics through a reaction intermediate that resides in a deep potential energy well with respect to both reactants, can lead to a deuterium enrichment in cold molecular clouds and even at elevated temperatures of a few thousand K as present in circumstellar envelopes of carbon stars. We acknowledge that this route cannot lead to a deuterium fractionation of a factor of 10^3. However, if D1-acetylene is formed via an ion-molecule reaction scheme involving reaction (3), the present neutral-neutral mechanisms can actually amplify and propagate the isotopic fractionation even further.

In this context it is important to mention that the inherent reaction rates of dicarbon with acetylene have been measured and were found to be very fast, i.e., a few 10^{-10} cm^3 s^{-1} (Smith et al. 2006) in the temperature range of 15–250 K. It should be recalled that the Gottlieb et al. (1983) and Guelin et al. (1987) millimeter-wave spectra of the 1,3-butadiynyl radical assisted its identification in the circumstellar envelope of the dying carbon star IRC +10216 (CW Leo) (Guelin et al. 1987) via four emission doublets of the $N = 9 \rightarrow 8$, $10 \rightarrow 9$, $11 \rightarrow 10$, and $12 \rightarrow 11$ rotational transitions. A recent survey suggests column densities of $(5.6–9.4) \times 10^{15}$ cm^{-2}, 1 order of magnitude higher than the ubiquitous l-C_3H radical and about 25% more abundant than the ethynyl radical (HCC; $X^2\Sigma^+$) (Doty & Leung 1998). Although the butadiynyl radical and its D1-itotopomer were both identified in TMC-1 (Irvine et al. 1981; Friberg et al. 1980), CCCCD($X^2\Sigma^+$) could not be found in the circumstellar envelope of IRC +10216. However, our investigation suggests, since a deuterium enrichment in D1-1,3-butadynyl radical can occur over a broad temperature range from 10 to a few thousand kelvin, that CCCCD($X^2\Sigma^+$) should be present in the outflow of carbon stars such as of IRC +10216. Finally, future chemical models simulating the deuterium enrichment in cold molecular clouds should incorporate the reaction between singlet dicarbon molecules and D1-acetylene to investigate objectively the role of this reaction in the deuterium fractionation in CCCCD($X^2\Sigma^+$) via a bimolecular neutral-neutral collision compared to the hitherto postulated dissociative recombination process of an electron with the D1-diacetylene cation (reactions [7] and [8]):

$$C_4HD^+ + e^- \rightarrow CCCCH + D, \tag{7}$$

$$C_4HD^+ + e^- \rightarrow CCCCD + H. \tag{8}$$

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REFERENCES

Becke, A. D. 1993, J. Chem. Phys., 98, 5648

Bell, M. B., Avery, L. W., Matthews, H. E., Feldman, P. A., Watson, J. K. G., Madden, S. C., & Irvine, W. M. 1988, ApJ, 326, 924

Ceccarelli, C., Vastel, C., Tielens, A. G. G. M., Castets, A., Boogert, A. C. A., Loinard, L., & Caux, E. 2002, A&A, 381, L17

Combes, F., Boulanger, F., Encrenaz, P. J., Gerin, M., Bogey, M., Demuynck, C., & Destombes, J. L. 1985, A&A, 147, L25

Doty, S. D., & Leung, C. M. 1998, ApJ, 502, 898

Friberg, P., Hjalmarson, A., & Irvine, W. M. 1980, ApJ, 241, L99

Frisch, M. J., et al. 1998, Gaussian 98, (Pittsburgh: Gaussian, Inc.)

Gerin, M., Combes, F., Wlodarczak, G., Encrenaz, P., & Laurent, C. 1992, A&A, 253, L29

Gottlieb, C. A., Gottlieb, E. W., Thaddeus, P., & Kawamura, H. 1983, ApJ, 275, 916

Gu, X., Guo, Y., Kawamura, E., & Kaiser, R. I. 2006a, J. Vac. Science & Technology A, 24, 505

Gu, X., Guo, Y., Zhang, F., Mebel, A. M., & Kaiser, R. I. 2006b, Faraday Discuss., 133, 245

Guelin, M., Cernicharo, J., Navarro, S., Gottlieb, C. A., & Thaddeus, P. 1987, A&A, 182, L37

Hatchell, J. 2003, A&A, 403, L25

Henchman, M. J., et al. 1988, in Rate Coefficients in Astrochemistry, ed. T. J. Millar & D. A. Williams (Dordrecht: Kluwer), 201

Herbst, E. 1992, in Isotope Effects in Gas-Phase Chemistry, ed. J. A. Kaye (Washington: ACS), 358

———. 2003, Space Sci. Rev., 106, 293

Irvine, W. M., Hoglund, B., Friberg, P., Askne, J., & Ellder, J. 1981, ApJ, 248, L113

Irvine, W. M., & Knacke, R. F. 1989, in Origins and Evolution of Planetary and Satellite Atmospheres, ed. Atreya et al. (Tucson: Univ. Arizona Press), 3

Kaiser, R. I. 2002, Chem. Rev., 102, 1309

Kaiser, R. I., Balucani, N., Charkin, D. O., & Mebel, A. M. 2003, Chem. Phys. Lett., 382, 122

Kaiser, R. I., Ochsenfeld, C., Head-Gordon, M., & Lee, Y. T. 1999, ApJ, 510, 784

Kaiser, R. I., Ochsenfeld, C., Stranges, D., Head-Gordon, M., & Lee, Y. T. 1998, Faraday Discuss., 109, 183

Kaiser, R. I., et al. 2001, Faraday Discuss., 119, 51

Kislov, V. V., Nguyen, T. L., Mebel, A. M., Lin, S. H., & Smith, S. C. 2004, J. Chem. Phys., 120, 7008

Lee, C., Yang, W., & Parr, R. G. 1988, Phys. Rev. B, 37, 785

Maluendes, S. A., McLean, A. D., & Herbst, E. 1993, ApJ, 417, 181

Millar, T. J. 2003, Space Sci. Rev., 106, 73

Millar, T. J., & Brown, P. D. 1989, in The Physics and Chemistry of Interstellar Molecular Clouds, ed. G. Winnewisser & J. T. Armstrong (Berlin: Springer), 368

Millar, T. J., Farquhar, P. R. A., & Willacy, K. 1997, A&AS, 121, 139

Minh, Y. C., & van Dishoeck, E. F., ed. 2000, IAU Symp. 197, Astrochemistry: From Molecular Clouds to Planetary Systems (San Francisco: ASP)

Osamura, Y., Roberts, H., & Herbst, E. 2005, ApJ, 621, 348

Parise, B., Castets, A., Herbst, E., Caux, E., Ceccarelli, C., Mukhopadhyay, I., & Tielens, A. G. G. M. 2004, A&A, 416, 159

Parise, B., Ceccarelli, C., Tielens, A. G. G. M., Herbst, E., Lefloch, B., Caux, E., Castets, A., Mukhopadhyay, I., Pagani, L., & Loinard, L. 2002, A&A, 393, L49

Purvis, G. D., & Bartlett, R. J. 1982, J. Chem. Phys., 76, 1910

Roberts, H., Herbst, E., & Millar, T. J. 2002, MNRAS, 336, 283

———. 2004, A&A, 424, 905

Roberts, H., & Millar, T. J. 2000, A&A, 361, 388

Rodgers, S. D., & Charnley, S. B. 2002, Planet. Space Sci., 50, 1125

Saito, S., Ozeki, H., Ohishi, M., & Yamamoto, S. 2000, ApJ, 535, 227

Sandford, S. A. 2002, Planet. Space Sci., 50, 1145

Schmoltner, A. M. 1989, Ph.D. thesis, Univ. California, Berkeley

Smith, I. W. M., Sage, A. M., Donahua, N. M., Herbst, E., & Quan, D. 2006, Faraday Discuss., 133, 137

Steinfeld, J. I., Francisco, J. S., & Hase, W. L. 1999, in Chemical Kinetics and Dynamics (Upper Saddle River: Prentice-Hall)

Teyssier, D., Fosse, D., Gerin, M., Pety, J., Abergel, A., & Roueff, E. 2004a, A&A, 417, 135

Teyssier, D., Pety, J., Gerin, M., Fosse, D., Abergel, A., Roueff, E., & Joblin, C. 2004b, in Proc. 4th Cologne-Bonn-Zermatt Symp., ed. S. Pfalzner et al. (Berlin: Springer), 521

Turner, B. E. 1989, ApJ, 347, L39

van der Tak, F. F. S., Schilke, P., Mueller, H. S. P., Lis, D. C., Phillips, T. G., Gerin, M., & Roueff, E. 2002, A&A, 388, L53

van Dishoek, E. F., et al. 1995, ApJ, 447, 760

Vastel, C., Phillips, T. G., Ceccarelli, C., & Pearson, J. 2003, ApJ, 593, L97

Vastel, C., Phillips, T. G., & Yoshida, H. 2004, ApJ, 606, L127

Vernon, M. 1981, Ph.D. thesis, Univ. California, Berkeley

Vrtilek, J. M., et al. 1985, ApJ, 296, L35

Walmsley, C. M., Henkel, C., Jacq, T., & Baudry, A. 1989, in The Physics and Chemistry of Interstellar Molecular Clouds, ed. G. Winnewisser & J. T. Armstrong (Berlin: Springer), 107

Weiss, M. S. 1986, Ph.D. thesis, Univ. California, Berkeley