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DEUTERIUM FRACTIONATION IN DENSE INTERSTELLAR CLOUDS

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ABSTRACT

We have studied the pseudo–time-dependent gas-phase chemistry of deuterium fractionation in dense interstellar clouds having temperatures in the range 10–70 K. Models have been run with two sets of theoretically determined branching ratios for dissociative recombination reactions between polyatomic ions and electrons. According to our results, in cold clouds the major and most global source of fractionation is H_2D^+ and ions derived from it such as DCO^+ and H_2DO^+, while in warmer clouds, reactions of CH_2D^+, C_2HD^+, and associated species lead to significant fractionation even at 70 K. A comparison between our detailed results and the abundance ratios between deuterated and normal species observed in Orion and TMC-1 indicates that the older dissociative recombination branching ratios, in which one or two hydrogen atoms are preferentially ejected from the parent neutral, lead to better agreement at 70 K (the assumed Orion temperature) than do the newer branching ratios, which are derived from the ideas of Bates. At lower temperatures the two sets of dissociative recombination branching ratios lead to similar deuterium fractionation abundance ratios, which are in good agreement with observed values in TMC-1. In addition to the temperature dependence of fractionation, its time dependence has also been investigated. In general the time dependence is not dramatic at low temperatures. At higher temperatures, the $[DCO^+]/[HCO^+]$ abundance ratio does vary strongly with time. Species deuterated principally by DCO^+ also show this time dependence. Indeed, the $[DCO^+]/[HCO^+]$ abundance ratio observed toward Orion is evidence that a chemical steady state has not been reached in this source.

Subject headings: deuterium — interstellar: molecules — nebulae: Orion Nebula

I. INTRODUCTION

In recent years molecules of increasing complexity have been detected in interstellar clouds, and theoretical models have been developed to understand the detailed chemical processes involving these species in such regions. For example, the recent model of Herbst and Leung (1989) considers molecules as complex as HC_9N. However successful such models may be, it is also important to be able to account for simple species. A particularly neglected set of such species are those containing deuterium atoms. With the notable exception of papers by Brown and Rice (1981, 1986), there has been no attempt to include deuterium chemistry in a comprehensive chemical model of interstellar clouds, although Langer *et al.* (1984) studied fractionation of carbon and oxygen. It is difficult to understand this neglect. Certainly, early papers by Langer and coworkers (Langer *et al.* 1979; Guélin, Langer, and Wilson 1982) showed an appreciation of the complexity of deuterium fractionation. Perhaps the answer lies in the fact that for some molecules such as HCO^+ the steady state abundance ratio between the deuterated and normal species can be estimated rather easily and independently of any detailed model (Watson 1976, 1977; Guélin *et al.* 1977; Snyder *et al.* 1977; Herbst 1982) from the $[H_2D^+]/[H_3^+]$ abundance ratio, which itself can be easily calculated from the $[HD]/[H_2]$ abundance ratio. In recent years, however, the complexity of deuterium fractionation has been well recognized by many scientists. Dalgarno and Lepp (1984) and Croswell and Dalgarno (1985) have pointed out the process of fractionation by D atoms derived from DCO^+ in cold clouds. Loren and Wootten (1985) and Wootten (1987) have reemphasized the importance of CH_2D^+, first discussed by Watson (1976), in the formation of DCN and HDCO in warm clouds. New theoretical models (Bell *et al.* 1986, 1988; Herbst *et al.* 1987) developed to understand the observed abundance ratios for [CCD]/[CCH] (Combes *et al.* 1985; Vrtilek *et al.* 1985) and $[C_3HD]/[C_3H_2]$ (Bell *et al.* 1986; Gerin *et al.* 1987) are complex and make several assumptions in order to lead to simple calculations. The fundamental problem is that it can be shown for these species that it is not possible in the analysis of deuterium fractionation to decouple a few reactions from the much larger set of reactions governing the hydrocarbon chemistry. This statement is true despite the fact that, according to current knowledge, all deuterium fractionation stems ultimately from the large reservoir of deuterium found in HD via exchange reactions between the ions H_3^+, CH_3^+, and $C_2H_2^+$ and HD. Besides the increasing realization that deuterium fractionation is more complex than originally believed because of the propagation and interconnection of the various mechanisms, there is also the problem of time dependence. While almost all fractionation calculations have utilized steady state conditions, "early-time" abundances ($t \approx 3 \times 10^5$ yr) seem to agree best with observed abundances for many species in dense interstellar clouds (Leung, Herbst, and Huebner 1984; Herbst and Leung 1986*a*).

For these reasons we report the results of a pseudo–time-dependent model of deuterium chemistry in dense clouds. Our approach has similarities to that of Brown and Rice (1986) but

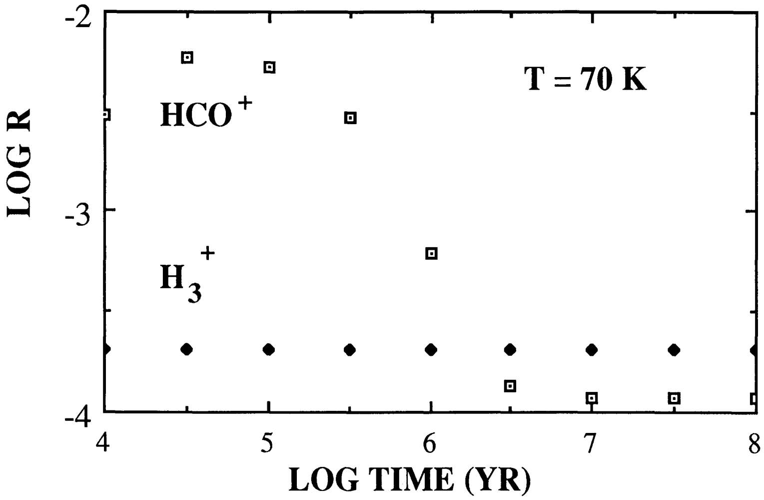

FIG. 1.—Logarithm of the calculated abundance ratio R between the deuterated and normal isotopes of a molecule, plotted against the logarithm of time for the species HCO^+ and H_3^+ in a cloud at 70 K. The "old" dissociative recombination branching ratios are utilized.

differs in certain respects. In particular, our chemistry involves species much more complex than those considered by Brown and Rice, uses more deuterium fractionation reactions including important radiative association reactions involving HD, and includes the use of new branching ratios for dissociative recombination reactions (Bates 1986*a*, 1987*a*; Millar *et al.* 1988). Also, we have used the detailed analysis of Herbst (1982) and Smith, Adams, and Alge (1982*a*) to calculate the rate of the H_3^+–HD exchange reaction as a function of temperature. Failure to use this detailed analysis can lead to significant error (Herbst 1982).

In order to see why a time-dependent calculation is required, consider the $[DCO^+]/[HCO^+]$ abundance ratio which is predicted from simple arguments to be approximately one-third that of $[H_2D^+]/[H_3^+]$. Our detailed results show that this is true at 10 K, when the $[H_2D^+]/[H_3^+]$ abundance ratio is large, but that the relationship does not hold at times earlier than steady state when the cloud temperature is greater than 30 K. Figure 1 shows the $[DCO^+]/[HCO^+]$ and $[H_2D^+]/[H_3^+]$ ratios as functions of time for $T = 70$ K. [In this and subsequent figures the abundance ratio is labeled R(AH), where AH is the normal species.] It can be seen that $R(HCO^+)$ is much larger at early times than at steady state. Clearly the time dependence of fractionation can be important—a point we return to later in more detail.

The remainder of the paper is organized as follows. In § II we discusss our reaction library, whereas in § III we describe our model calculations and present our detailed results. In § IV we discuss these results with particular emphasis on the time dependence and temperature dependence of the abundance ratios R(AH) for various species AH. We also contrast the results of calculations which use the new idea of Bates (1986*a*, 1987*a*) in determining the branching ratios of dissociative recombination reactions as quantified by Millar *et al.* (1988) with the results of calculations which utilize older ideas concerning these branching ratios. Our calculated ratios R(AH) are compared with observed values in Orion, a high-temperature cloud, and with those in TMC-1, a cold interstellar cloud, in § V. A comparison with the previous work of Brown and Rice (1986) is included in § VI. Finally, our conclusions are presented in § VII.

II. REACTION LIBRARY

The basic chemical model used (Millar *et al.* 1988) has been developed over a period of time and describes the chemistry of dense interstellar clouds in a pseudo–time-dependent manner, in which abundances evolve chemically from initial values under fixed physical conditions. With the exception of H_2 which forms on grain surfaces, only gas-phase processes are involved. We have used computer software described by Bennett (1988) to extend the chemistry to include all the monodeuterated analogs of hydrogen-bearing species. This inclusion increases the number of gas-phase reactions appreciably, since, for many reactions, several product channels are possible. For example, the reaction

$$C_3^+ + H_2 \rightarrow C_3H^+ + H \tag{1}$$

has two sets of products when C_3^+ reacts with HD:

$$C_3^+ + HD \rightarrow C_3H^+ + D\ , \tag{2}$$

$$C_3^+ + HD \rightarrow C_3D^+ + H\ . \tag{3}$$

For normal exothermic ion-molecule reactions we have assumed that the total rate coefficient is unchanged for deuterium analogs, e.g., $k_1 = k_2 + k_3$, and have also assumed statistical branching ratios, e.g., $k_2 = k_3 = k_1/2$. The first assumption is a reasonable one, since for all exothermic ion-molecule reactions in our model there is no significant activation energy barrier, and only small adjustments in rate due to reduced mass effects exist. The existence of a barrier, however, normally leads to important isotopic differences in rate. The second assumption is made for simplicity and lack of experimental evidence. Phase-space theory calculations indicate that for exothermic ion-molecule reactions, favored products are those with greater exothermicities and more closely spaced energy levels (Herbst 1978). Thus, in reactions (2) and (3), C_3D^+ might be expected to be favored to some degree over its hydrogen analog. However, phase-space theory is an approximate treatment, and it is not even feasible to attempt such calculations given the scope of our model and the lack of knowledge of the positions of the energy levels of most polyatomic ions.

Besides exothermic ion-molecule reactions, we have generated dissociative recombination reaction rate coefficients for monodeuterated ions using the same rate coefficients as the analogous hydrogen-based ions and the "statistical" approximation for branching ratios. Our "statistical" approximation does not refer to the phase-space calculations of Herbst (1978) but to the idea that hydrogen and deuterium atoms have equal probability of being produced. This statistical approximation has recently been questioned by Bell *et al.* (1988), who noted in their observational study of C_3HD that Gellene and Porter (1983, 1984) determined that for metastable neutrals formed by recombination in ion beam experiments H atom loss occurs preferentially. The difference between the statistical viewpoint and the Gellene-Porter results can be shown for the ion ND_3H^+. Statistically one expects that upon neutral formation followed by dissociation in which one hydrogen or deuterium atom is removed, the chance of removing a D atom would be 3 times the chance of removing an H atom. However, Gellene and Porter (1984) found an 8:1 preferential loss in favor of H and theorized that the cause of the effect was a tunneling dissociation mechanism in which H atoms are the more efficient. It should be noted that their experiment produces metastable and unstable neutrals from reactions between ions and sodium and/or potassium atoms and that their results may not be applicable directly to unstable parent neutrals formed via recombination of ions and electrons. The statistical approximation results in less deuterium fractionation of the product neutral than does a mechanism in which H removal dominates (Bell *et al.* 1988).

In addition to the many reactions generated by the software (a list is available from T. J. M.), we have supplemented our reaction set with a number of fractionation reactions involving D, HD, H_2D^+, CH_2D^+, and C_2HD^+. These reactions and the adopted rate coefficients are shown in Table 1. At low temperatures the most prevalent fractionation reaction is

$$H_3^+ + HD \underset{k_r}{\overset{k_f}{\rightleftarrows}} H_2D^+ + H_2 , \tag{4}$$

where the left-to-right reaction is the exothermic one and

$$k_r = k_f \exp\,[\Delta G(T)/T] , \tag{5}$$

where ΔG, the free-energy change in K for the exothermic reaction, can be subdivided into entropy (ΔS) and enthalpy (ΔH) contributions via the relation $\Delta G = \Delta H - T\,\Delta S$, leading to the equation

$$k_r = k_f \exp\,[-\Delta S]\,\exp\,[+\Delta H/T] . \tag{6}$$

Note that ΔH is negative in this convention. For most important fractionation reactions, the absolute value of the enthalpy change is sufficiently large that the temperature dependence of the thermodynamic parameters is not serious. However, the small size of the enthalpy change for reaction (4) renders its temperature dependence quite significant at interstellar cloud temperatures (Herbst 1982; Smith, Adams, and Alge 1982*a*), and it must be considered in any rigorous treatment of fractionation via reaction (4). We have listed values for k_f and k_r at four temperatures—10, 30, 50, and 70 K—in Table 1. The forward (exothermic) rate coefficient is assumed to occur at a near-Langevin value, since a variety of measurements (see, e.g., Adams and Smith 1981) show that this and analogous exothermic isotopic fractionation rate coefficients approach the Langevin value at low temperatures. The endothermic reverse rate coefficient is then calculated via equation (5) or equation (6) with the additional assumption that nonthermal effects are unimportant (Herbst 1982).

There are a variety of other fractionation reactions involving HD in Table 1. The most important of these involve the hydrocarbon ions CH_3^+ and $C_2H_2^+$.

$$CH_3^+ + HD \leftrightarrows CH_2D^+ + H_2 , \tag{7}$$

$$C_2H_2^+ + HD \leftrightarrows C_2HD^+ + H_2 . \tag{8}$$

In these systems, the reaction enthalpy, determined either experimentally or via zero-point energy differences, is sufficiently large ($\Delta H_7 = -370$ K and $\Delta H_8 \approx -550$ K) that its temperature dependence and that of ΔS can be neglected without serious consequences. The rate coefficient k_r of the reverse (endothermic) reaction is then easily computed and has the form $A \exp\,(-B/T)$ once the assumption that k_f is independent of temperature has been made. The large size of the reaction enthalpy makes these fractionation reactions important at far higher temperatures than reaction (4), since the backward endothermic reaction with H_2 is slower (see eq. [6]), as has been noted (Combes *et al.* 1985; Wootten 1987; Herbst *et al.* 1987). We have not included any other fractionation reactions involving hydrocarbon ions and HD because there is no experimental evidence on this point. To be important in HD fractionation, a hydrocarbon ion must not react *rapidly* with H_2, else it would possess too small an abundance. Yet it should react *slowly* with H_2, say via radiative or ternary association, because such a reaction with H_2 is evidence that the ion and H_2 can form a temporary collision complex and therefore do not possess an activation energy barrier in the entrance channel, a probable necessary condition for reaction with HD. Both CH_3^+ and $C_2H_2^+$ (as well as H_3^+) obey these constraints; we are not aware of any other hydrocarbon ion that does so.

In addition to the fractionation reactions involving HD, we have included processes involving deuterium atoms in Table 1. These processes can be subdivided into ion-atom and neutral-atom reactions. The ion-atom reactions (e.g., $D + H_3^+$) are sufficiently exothermic (large enthalpy change) that estimation of forward and backward rate coefficients is simple. The one important neutral-atom reaction considered is the $D + OH = OD + H$ system (Croswell and Dalgarno 1985). We note that we have neglected the possible fractionation of the radical CCH by D atoms, since such a process is very efficient at low temperatures and would lead to a [CCD]/[CCH] abundance ratio in TMC-1 much larger than that observed. It is therefore probable that the CCH + D reaction has at least a small activation energy. It is likely that the CCH + O reaction has a small activation energy barrier in order to account for the observed abundance of CCH in cold clouds; the assumption that CCH + D also has a barrier seems reasonable.

In Table 1 there are also listed several radiative association reactions involving either deuterated ions or neutrals that are important in our fractionation scheme and strongly affect the temperature dependence of fractionation (Herbst *et al.* 1987). For these systems, e.g.,

$$CH_2D^+ + H_2 \rightarrow CH_4D^+ + h\nu , \tag{9}$$

total rate coefficients are not preserved in our model, because according to both theoretical (Herbst *et al.* 1987; Bates 1986*b*, 1987*b*) and experimental (Smith, Adams, and Alge 1982*b*) treatments, association reactions involving deuterated species do not occur with the same rate coefficient as their hydrogen analogs. We have used a combination of theoretical and experimental work to derive the radiative association rate coefficients shown in Table 1. If there is no competitive exothermic channel, the rate coefficients for association reactions involving a monodeuterated species typically exceed those for the hydrogen analogs, but only by small factors. The existence of competitive exothermic channels, however, can reduce association rate coefficients to negligible values (see, e.g., $CH_3^+ + HD \rightarrow CH_4D^+$ in Table 1) or only by minor amounts depending on the potential surface of the reactions (Herbst 1987).

The adopted rate coefficients for the radiative association reactions leading to the monodeuterated isotopes of protonated methanol require special comment. In our calculations

TABLE 1

PRIMARY DEUTERATION REACTIONS AND THEIR RATE COEFFICIENTS BETWEEN 10 AND 70 K

A. $H_3^+ + HD \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H_2D^+ + H_2$

Reaction	Rate Coefficient k (cm^3 s^{-1}) 10 K	30 K	50 K	70 K	Reference
$H_3^+ + HD \rightarrow H_2D^+ + H_2$	1.7(−09)	1.5(−09)	1.5(−09)	1.4(−09)	SAA*
$H_2D^+ + H_2 \rightarrow H_3^+ + HD$	3.6(−18)	8.8(−12)	9.3(−11)	2.0(−10)	H

B. $k = A \exp(-B/T)$

Reaction	Rate Coefficient k (cm^3 s^{-1}) A (cm^3 s^{-1})	B (K)	Reference
$CH_3^+ + HD \rightarrow CH_2D^+ + H_2$	1.3(−09)	...	SAA*
$CH_2D^+ + H_2 \rightarrow CH_3^+ + HD$	8.7(−10)	370	SAA*
$C_2H_2^+ + HD \rightarrow C_2HD^+ + H_2$	1.0(−09)	...	HASD
$C_2HD^+ + H_2 \rightarrow C_2H_2^+ + HD$	2.5(−09)	550	HASD
$D^+ + H_2 \rightarrow H^+ + HD$	2.1(−09)	...	SAA*
$H^+ + HD \rightarrow D^+ + H_2$	1.0(−09)	464	SAA*
$D^+ + H \rightarrow H^+ + D$	1.0(−09)	...	W*
$H^+ + D \rightarrow D^+ + H$	1.0(−09)	41	W*
$H_3^+ + D \rightarrow H_2D^+ + H$	1.0(−09)	...	Estimate by AS
$H_2D^+ + H \rightarrow H_3^+ + D$	1.0(−09)	632	Estimate by AS
$HCO^+ + D \rightarrow DCO^+ + H$	1.0(−09)	...	AS*
$DCO^+ + H \rightarrow HCO^+ + D$	2.2(−09)	796	AS*
$HN_2^+ + D \rightarrow DN_2^+ + H$	1.0(−09)	...	AS*
$DN_2^+ + H \rightarrow HN_2^+ + D$	2.2(−09)	550	AS*
$OH + D \rightarrow OD + H$	1.3(−10)	...	CD
$OD + H \rightarrow OH + D$	1.3(−10)	810	CD

C. $k = A(T/10\ K)^{-C}$

Reaction	Rate Coefficient k (cm^3 s^{-1}) A (cm^3 s^{-1})	C	Reference
$CH_3^+ + HD \rightarrow CH_4D^+ + h\nu$	0.0	...	SAA
$CH_2D^+ + H_2 \rightarrow CH_4D^+ + h\nu$	6.0(−12)	0.5	This work; based on B and SAA
$C_2H_2^+ + HD \rightarrow C_2H_3D^+ + h\nu$	0.0	...	HASD
$C_2HD^+ + H_2 \rightarrow C_2H_3D^+ + h\nu$	6.5(−13)	1.0	HASD, HE
$CH_2D^+ + H_2O \rightarrow CH_2DOH_2^+ + h\nu$	3.0(−10)	1.7	This work
$CH_3^+ + HDO \rightarrow CH_3OHD^+ + h\nu$	3.0(−09)	1.7	This work

NOTES.—The entries in the table follow the convention $a(-b)$ signifies $a \times 10^{-b}$. An asterisk in the Reference column indicates that the reaction was also included by Brown and Rice 1986 at roughly the same rate.

REFERENCES.—SAA: Smith, Adams, and Alge 1982*a*, *b*; H: Herbst 1982; HASD: Herbst *et al.* 1987; W: Watson 1976; AS: Adams and Smith 1985; CD: Croswell and Dalgarno 1985; B: Bates 1987*a*; HE: Herbst 1985.

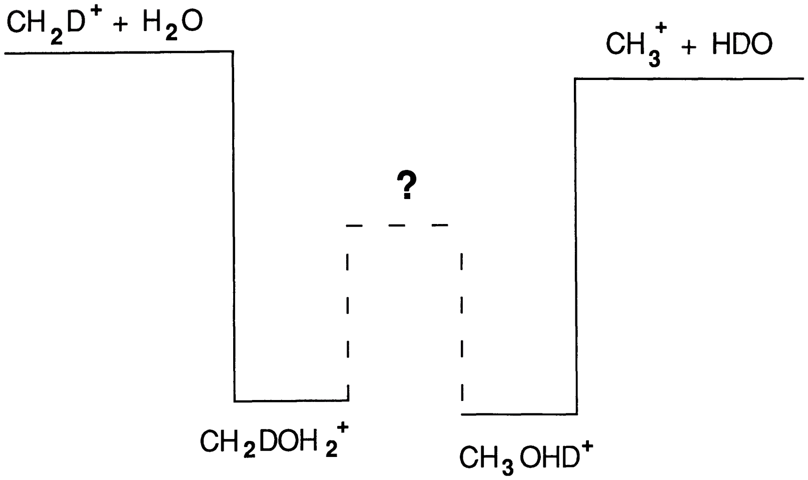

FIG. 2.—Schematic view of the potential surface connecting $CH_2D^+ + H_2O$ with $CH_3^+ + HDO$. The height of the transition state is unknown and is indicated by a question mark.

we have assumed that the radiative association reactions

$$CH_3^+ + HDO \rightarrow CH_3OHD^+ + h\nu \quad (10)$$

and

$$CH_2D^+ + H_2O \rightarrow CH_2DOH_2^+ + h\nu \quad (11)$$

both occur and lead to the neutrals CH_3OD and CH_2DOH, respectively, via dissociative recombination reactions. We have assumed that reaction (10) occurs more rapidly than reaction (11) because the exothermic reaction

$$CH_2D^+ + H_2O \rightarrow CH_3^+ + HDO \quad (12)$$

($\Delta H \approx -130$ K) probably competes with reaction (11). However, it is not clear that reaction (12) occurs efficiently, nor is it clear that reactions (10) and (11) produce the products indicated above. The confused situation is represented in Figure 2. If the barrier between the ions $CH_2DOH_2^+$ and CH_3OHD^+ is reasonably low, then when these ions are formed from either set of reactants ($CH_2D^+ + H_2O$ or $CH_3^+ + HDO$) the ions may rapidly equilibrate ("deuterium shuffling") until enough energy is lost through radiation that isomerization can no longer occur. The net result will be the formation of both species with approximately the same branching ratio. On the other hand, if the barrier between the two deuterated isotopic ions is large, then reactions (10) and (11) will indeed produce separate and distinct product ions. In this limit, it is unclear whether reaction (12) can proceed—this reaction could not proceed through the slice of the multidimensional potential surface shown in Figure 2, because of the high barrier.

In the absence of detailed information on reactions (10)–(12), we present our abundances of deuterated methanol and its protonated ion as the sums of CH_2DOH and CH_3OD and of $CH_2DOH_2^+$ and CH_3OHD^+, respectively. A detailed investigation such as that carried out on the CH_3^+–HCN system by DeFrees, McLean, and Herbst (1985) is required.

III. MODEL CALCULATIONS

We have performed a pseudo–time-dependent calculation for 225 species linked by approximately 1700 reactions. The fixed physical conditions are $n(H_2) = 10^4$ cm^{-3}, $A_V = 10$ mag, and temperatures of 10, 30, 50, and 70 K. Hydrogen is assumed to be initially in its molecular form with the initial $[HD]/H_2$ abundance ratio set to 3×10^{-5}. We have neglected the effects of enhanced rate coefficients in ion-polar neutral reactions, since their effects are not usually large (Herbst and Leung 1986*b*), and, in addition, enhanced rate coefficients do not always occur where expected (Rowe 1988). We have also neglected the influence of cosmic-ray–induced UV photons because their effects are not great, particularly at early times (Millar 1988; Gredel *et al.* 1989). Finally, we have neglected the chemistry of species of polycyclic aromatic hydrocarbon (PAH) type and their interaction with smaller molecules because their presence in cold dense clouds is still a matter of conjecture. We have, however, calculated models for both "old" and "new" dissociative recombination branching ratios, so that, in total, the results of eight models will be presented. The "old" dissociative recombination branching ratios refer to the view that ejection of single and multiple hydrogen atoms is favored to the breaking of heavy atom–heavy atom bonds, whereas the "new" ratios are based on the opposing view of Bates (1986*a*, 1987*a*) as interpreted by Millar *et al.* (1988). A discussion can be found in Bates and Herbst (1988).

Because this paper concerns deuterium fractionation, we do not present calculated absolute abundances of the molecular species in our model. It is to be noted, though, that the calculated abundances are similar to those of previous models in this class (see Millar, Leung, and Herbst 1987) and show, for all of the more complex species in the model, the normal pattern in which most abundances peak at an early time ($\approx 3 \times 10^5$ yr) before declining as steady state is reached. Since complexity-destroying oxygen atom reactions are included in the model, the steady state abundances of complex molecules are normally orders of magnitude below observed values (Millar, Leung, and Herbst 1987).

In Table 2 are listed calculated abundance ratios of deuterated to hydrogenated species; i.e., $R(AH) \equiv [AD]/[AH]$. Results are presented at various temperatures both for "early time" (3.16×10^5 yr), when the abundances of most complex molecules are at or near their peak values, and for steady state (10^8 yr). The results have been obtained using the "old" dissociative recombination branching ratios. In Table 3 similar

TABLE 2

Selected Calculated Ratios of Deuterated to Normal Abundances Obtained with "Old" Recombination Branching Ratios

Chemical	Temperature (K)							
	10 K		30 K		50 K		70 K	
Species	Early	St. State	Early	St. State	Early	St. State	Early	St. State
H	4.9(-03)	1.6(-02)	1.2(-03)	6.8(-04)	1.2(-03)	8.9(-05)	1.4(-03)	5.1(-05)
H_2	2.9(-05)	2.8(-05)	3.0(-05)	3.0(-05)	3.0(-05)	3.0(-05)	3.0(-05)	3.0(-05)
CH	1.5(-02)	3.4(-02)	1.2(-02)	1.1(-02)	1.7(-02)	1.4(-02)	2.1(-02)	1.8(-02)
NH	1.3(-03)	4.4(-03)	1.7(-04)	1.8(-04)	1.4(-04)	3.2(-05)	1.7(-04)	2.3(-05)
OH	4.7(-02)	5.9(-01)	4.3(-03)	9.1(-03)	2.8(-03)	7.4(-04)	2.4(-03)	3.2(-04)
CH_2	4.5(-03)	1.1(-02)	3.7(-03)	4.5(-03)	5.4(-03)	5.4(-03)	6.8(-03)	6.3(-03)
NH_2	2.7(-03)	9.1(-03)	3.4(-04)	3.6(-04)	2.9(-04)	6.4(-05)	3.5(-04)	4.6(-05)
H_2O	2.1(-02)	3.1(-02)	2.4(-03)	9.7(-04)	1.6(-03)	1.2(-04)	1.6(-03)	6.8(-05)
HCN	1.1(-02)	4.3(-02)	2.3(-03)	1.7(-03)	2.7(-03)	9.2(-04)	3.5(-03)	1.2(-03)
HNC	1.8(-02)	1.8(-02)	2.6(-03)	6.6(-04)	2.3(-03)	1.3(-04)	2.8(-03)	1.3(-04)
HCO	2.8(-02)	5.5(-02)	6.1(-03)	4.8(-03)	6.8(-03)	4.0(-03)	7.5(-03)	4.5(-03)
C_2H	1.4(-02)	3.4(-02)	9.2(-03)	1.1(-02)	1.2(-02)	1.3(-02)	1.4(-02)	1.6(-02)
NH_3	3.4(-03)	1.5(-02)	4.8(-04)	5.5(-04)	4.3(-04)	9.7(-05)	5.4(-04)	6.9(-05)
CH_3	3.8(-02)	6.0(-02)	2.1(-02)	1.5(-02)	2.7(-02)	1.7(-02)	3.2(-02)	1.9(-02)
C_2H_2	2.4(-02)	6.7(-02)	2.3(-02)	2.5(-02)	2.7(-02)	2.8(-02)	2.9(-02)	3.1(-02)
C_3H	1.1(-02)	4.0(-02)	6.8(-03)	5.0(-03)	7.2(-03)	5.2(-03)	7.6(-03)	6.4(-03)
H_2CO	3.2(-02)	6.4(-02)	1.3(-02)	1.0(-02)	1.5(-02)	1.0(-02)	1.9(-02)	1.2(-02)
CH_4	3.9(-02)	8.8(-02)	2.0(-02)	1.9(-02)	2.4(-02)	2.0(-02)	2.7(-02)	2.3(-02)
C_2H_3	4.4(-02)	8.6(-02)	7.0(-02)	1.2(-01)	8.4(-02)	1.7(-01)	9.1(-02)	2.1(-01)
C_3H_2	1.2(-02)	3.2(-02)	1.3(-02)	4.6(-03)	1.3(-02)	5.0(-03)	1.5(-02)	5.9(-03)
C_4H	1.3(-02)	5.1(-02)	5.8(-03)	4.5(-03)	5.5(-03)	3.0(-03)	5.9(-03)	3.0(-03)
CH_2CO	3.3(-02)	7.1(-02)	4.6(-02)	5.6(-02)	6.1(-02)	7.7(-02)	7.2(-02)	9.4(-02)
HC_3N	1.9(-02)	4.9(-02)	3.4(-03)	2.1(-03)	2.8(-03)	6.0(-04)	2.3(-03)	5.6(-04)
C_3H_3	3.3(-02)	9.1(-02)	2.8(-02)	2.5(-02)	3.5(-02)	3.1(-02)	4.1(-02)	3.7(-02)
C_4H_2	2.6(-02)	8.6(-02)	2.1(-02)	2.3(-02)	2.5(-02)	2.8(-02)	2.9(-02)	3.4(-02)
CH_3OH^a	4.5(-02)	1.1(-01)	8.3(-03)	5.0(-03)	8.5(-03)	2.1(-03)	1.1(-02)	2.2(-03)
CH_3CN	2.3(-02)	7.0(-02)	1.0(-02)	7.0(-03)	1.2(-02)	4.1(-03)	1.4(-02)	4.8(-03)
C_3H_4	4.5(-02)	1.2(-01)	3.7(-02)	3.3(-02)	4.7(-02)	4.1(-02)	5.5(-02)	5.1(-02)
HC_5N	2.0(-02)	3.9(-02)	6.5(-03)	1.4(-03)	6.2(-03)	2.2(-04)	6.4(-03)	1.5(-04)
H_3^+	1.1(-01)	1.6(-01)	4.8(-03)	4.9(-03)	4.8(-04)	4.8(-04)	2.0(-04)	2.1(-04)
HCO^+	3.1(-02)	5.4(-02)	3.4(-03)	2.1(-03)	2.6(-03)	2.3(-04)	3.0(-03)	1.2(-04)
N_2H^+	3.3(-02)	4.9(-02)	1.9(-03)	1.7(-03)	4.6(-04)	1.7(-04)	3.8(-04)	7.5(-05)
CH_3^+	2.1(-02)	1.3(-02)	1.5(-02)	1.3(-02)	1.9(-02)	1.6(-02)	2.4(-02)	1.9(-02)
H_3O^+	3.7(-02)	4.4(-02)	3.4(-03)	1.5(-03)	2.0(-03)	1.8(-04)	2.0(-03)	1.0(-04)
$C_2H_2^+$	4.9(-02)	8.1(-02)	9.7(-02)	1.2(-01)	1.4(-01)	1.7(-01)	1.7(-01)	2.2(-01)
$HCNH^+$	5.4(-02)	8.6(-02)	5.4(-03)	3.1(-03)	4.5(-03)	5.9(-04)	5.5(-03)	5.6(-04)
C_3H^+	1.0(-02)	2.1(-02)	8.1(-03)	6.9(-03)	9.4(-03)	8.6(-03)	1.0(-02)	1.0(-02)
NH_4^+	5.5(-03)	1.8(-02)	6.9(-04)	7.3(-04)	5.8(-04)	1.3(-04)	7.0(-04)	9.2(-05)
$C_2H_3^+$	3.9(-02)	1.0(-01)	1.9(-02)	2.3(-02)	2.2(-02)	2.4(-02)	2.5(-02)	2.7(-02)
$C_3H_2^+$	3.4(-02)	9.2(-02)	1.2(-02)	1.1(-02)	1.2(-02)	1.1(-02)	1.2(-02)	1.3(-02)
CH_5^+	6.5(-02)	1.0(-01)	2.6(-02)	2.3(-02)	2.9(-02)	2.5(-02)	3.4(-02)	2.9(-02)
$C_2H_4^+$	7.1(-02)	1.2(-01)	1.3(-01)	1.6(-01)	1.9(-01)	2.4(-01)	2.2(-01)	3.0(-01)
$C_3H_3^+$	2.0(-02)	4.5(-02)	1.2(-02)	6.9(-03)	1.3(-02)	7.3(-03)	1.4(-02)	8.6(-03)
HC_3NH^+	4.1(-02)	9.4(-02)	6.2(-03)	4.2(-03)	5.0(-03)	1.2(-03)	5.4(-03)	1.1(-03)
$C_3H_4^+$	6.6(-02)	1.5(-01)	4.3(-02)	3.2(-02)	5.2(-02)	3.8(-02)	6.1(-02)	4.7(-02)
$C_4H_3^+$	5.0(-02)	1.2(-01)	2.8(-02)	3.5(-02)	3.4(-02)	4.3(-02)	3.8(-02)	5.2(-02)
$CH_3OH_2^{+\,b}$	5.3(-02)	9.1(-02)	7.3(-03)	3.1(-03)	6.5(-03)	3.7(-04)	7.9(-03)	2.1(-04)
CH_3CNH^+	4.1(-02)	9.2(-02)	1.3(-02)	9.0(-03)	1.4(-02)	5.4(-03)	1.7(-02)	6.3(-03)

Note.—All numbers in the table follow the convention $a(-b)$ signifies $a \times 10^{-b}$.

[a] The abundances of the deuterated species CH_3OD and CH_2DOH are added together (see text).

[b] The abundances of the deuterated species CH_3OHD^+ and $CH_2DOH_2^+$ are added together (see text).

TABLE 3

Selected Calculated Ratios of Deuterated to Normal Abundances Obtained with "New" Recombination Branching Ratios

Chemical Species	10 K Early	10 K St. State	30 K Early	30 K St. State	50 K Early	50 K St. State	70 K Early	70 K St. State
H	3.9(-03)	8.0(-03)	9.9(-04)	8.5(-04)	7.9(-04)	1.0(-04)	3.5(-04)	4.9(-05)
H_2	2.8(-05)	2.5(-05)	2.9(-05)	3.0(-05)	3.0(-05)	3.0(-05)	3.0(-05)	3.0(-05)
CH	1.1(-02)	1.1(-02)	1.2(-02)	1.1(-02)	1.4(-02)	1.3(-02)	4.6(-03)	3.7(-03)
NH	1.1(-02)	2.2(-02)	4.8(-03)	2.9(-03)	5.0(-03)	3.8(-04)	2.0(-03)	1.8(-04)
OH	3.7(-02)	1.0(-01)	6.5(-03)	6.1(-03)	5.0(-03)	1.1(-03)	2.0(-03)	3.8(-04)
CH_2	1.4(-02)	1.8(-02)	6.9(-03)	9.9(-03)	6.4(-03)	9.1(-03)	2.8(-03)	3.2(-03)
NH_2	9.9(-03)	6.2(-02)	7.4(-03)	8.1(-03)	7.6(-03)	1.0(-03)	3.7(-03)	4.9(-04)
H_2O	2.8(-02)	3.8(-02)	4.1(-03)	3.7(-03)	2.7(-03)	4.1(-04)	1.3(-03)	1.8(-04)
HCN	1.2(-02)	2.2(-02)	3.2(-03)	2.7(-03)	2.7(-03)	1.0(-03)	1.2(-03)	3.8(-04)
HNC	1.9(-02)	2.3(-02)	3.0(-03)	2.4(-03)	2.0(-03)	4.4(-04)	9.2(-04)	1.7(-04)
HCO	7.0(-03)	1.1(-02)	3.5(-03)	4.3(-03)	3.3(-03)	3.7(-03)	1.4(-03)	1.3(-03)
C_2H	1.1(-02)	1.1(-02)	9.3(-03)	8.5(-03)	9.9(-03)	1.0(-02)	3.3(-03)	2.8(-03)
NH_3	1.3(-02)	1.0(-01)	1.9(-03)	1.3(-02)	1.3(-03)	1.6(-03)	6.6(-04)	7.3(-04)
CH_3	2.8(-02)	3.7(-02)	1.7(-02)	2.4(-02)	1.7(-02)	2.8(-02)	7.1(-03)	9.1(-03)
C_2H_2	1.7(-02)	1.3(-02)	2.9(-02)	4.0(-03)	3.5(-02)	2.9(-03)	1.2(-02)	1.1(-03)
C_3H	7.4(-03)	1.2(-02)	6.3(-03)	2.3(-03)	6.4(-03)	1.1(-03)	2.2(-03)	3.2(-04)
H_2CO	2.4(-02)	3.3(-02)	1.1(-02)	1.4(-02)	9.9(-03)	1.4(-02)	4.3(-03)	4.6(-03)
CH_4	3.0(-02)	2.9(-02)	1.8(-02)	1.5(-02)	1.8(-02)	1.3(-02)	8.7(-03)	6.2(-03)
C_2H_3	3.5(-02)	5.7(-02)	5.8(-02)	9.3(-02)	6.4(-02)	1.1(-01)	2.1(-02)	2.5(-02)
C_3H_2	1.0(-02)	1.3(-02)	1.5(-02)	2.1(-03)	1.7(-02)	1.2(-03)	6.2(-03)	4.5(-04)
C_4H	7.8(-03)	1.1(-02)	7.2(-03)	4.4(-03)	7.8(-03)	5.0(-03)	2.9(-03)	1.5(-03)
CH_2CO	2.7(-02)	3.8(-02)	3.9(-02)	5.2(-02)	4.3(-02)	6.0(-02)	1.4(-02)	1.5(-02)
HC_3N	9.1(-03)	9.3(-03)	5.9(-03)	1.5(-03)	6.2(-03)	6.5(-04)	2.2(-03)	2.2(-04)
C_3H_3	3.3(-02)	4.5(-02)	4.0(-02)	4.6(-02)	4.4(-02)	5.3(-02)	1.6(-02)	1.4(-02)
C_4H_2	2.3(-02)	2.6(-02)	7.0(-02)	1.5(-02)	2.7(-02)	1.6(-02)	1.0(-02)	4.3(-03)
CH_3OH[a]	4.6(-02)	8.0(-02)	8.7(-03)	1.2(-02)	6.9(-03)	6.8(-03)	3.4(-03)	3.5(-03)
CH_3CN	2.2(-02)	3.5(-02)	1.1(-02)	1.1(-02)	1.1(-02)	9.2(-03)	5.2(-03)	4.3(-03)
C_3H_4	4.3(-02)	5.2(-02)	4.7(-02)	3.2(-02)	5.3(-02)	3.6(-02)	2.0(-02)	1.2(-02)
HC_5N	1.3(-02)	1.3(-02)	1.0(-02)	2.3(-03)	1.1(-02)	1.1(-03)	4.0(-03)	3.5(-04)
H_3^+	6.8(-02)	4.6(-02)	4.6(-03)	4.5(-03)	4.7(-04)	4.8(-04)	2.0(-04)	2.1(-04)
HCO^+	1.9(-02)	1.8(-02)	2.9(-03)	1.7(-03)	1.9(-03)	1.9(-04)	8.4(-04)	8.1(-05)
N_2H^+	2.1(-02)	1.6(-02)	1.8(-03)	1.6(-03)	4.8(-04)	1.7(-04)	1.8(-04)	7.3(-05)
CH_3^+	1.6(-02)	1.0(-02)	1.2(-02)	1.2(-02)	1.2(-02)	1.3(-02)	5.8(-03)	5.9(-03)
H_3O^+	4.5(-02)	5.6(-02)	6.1(-03)	5.6(-03)	3.7(-03)	6.2(-04)	1.7(-03)	2.7(-04)
$C_2H_2^+$	3.7(-02)	4.3(-02)	7.1(-02)	1.0(-01)	8.2(-02)	1.2(-01)	2.4(-02)	2.7(-02)
$HCNH^+$	4.5(-02)	4.4(-02)	5.6(-03)	4.6(-03)	3.2(-03)	8.6(-04)	1.4(-03)	3.4(-04)
C_3H^+	8.5(-03)	6.5(-03)	1.1(-02)	2.0(-03)	1.3(-02)	1.5(-03)	4.5(-03)	5.5(-04)
NH_4^+	1.8(-02)	6.2(-02)	2.3(-03)	6.4(-03)	1.3(-03)	7.1(-04)	6.5(-04)	3.1(-04)
$C_2H_3^+$	3.3(-02)	3.2(-02)	2.1(-02)	8.1(-03)	2.2(-02)	5.5(-03)	9.1(-03)	2.4(-03)
$C_3H_2^+$	2.6(-02)	2.6(-02)	1.6(-02)	5.3(-03)	1.5(-02)	2.7(-03)	5.1(-03)	7.1(-04)
CH_5^+	4.1(-02)	4.0(-02)	2.3(-02)	2.1(-02)	2.3(-02)	1.9(-02)	1.1(-02)	8.8(-03)
$C_2H_4^+$	5.5(-02)	7.3(-02)	9.6(-02)	1.3(-01)	1.1(-01)	1.5(-01)	3.2(-02)	3.4(-02)
$C_3H_3^+$	2.1(-02)	1.9(-02)	2.2(-02)	3.2(-03)	2.4(-02)	1.8(-03)	7.8(-03)	6.5(-04)
HC_3NH^+	1.9(-02)	1.8(-02)	1.2(-02)	2.9(-03)	1.2(-02)	1.3(-03)	4.3(-03)	4.4(-04)
$C_3H_4^+$	4.5(-02)	5.8(-02)	5.5(-02)	6.2(-02)	6.2(-02)	7.2(-02)	2.1(-02)	1.9(-02)
$C_4H_3^+$	3.6(-02)	3.8(-02)	3.5(-02)	2.4(-02)	3.9(-02)	2.7(-02)	1.4(-02)	7.6(-03)
$CH_3OH_2^+$[b]	5.4(-02)	8.0(-02)	8.1(-03)	8.1(-03)	5.4(-03)	9.5(-04)	2.7(-03)	4.2(-04)
CH_3CNH^+	3.3(-02)	4.4(-02)	1.5(-02)	1.5(-02)	1.4(-02)	1.2(-02)	6.8(-03)	5.7(-03)

Note.—All numbers in the table follow the convention $a(-b)$ signifies $a \times 10^{-b}$.

[a] The abundances of the deuterated species CH_3OD and CH_2DOH are added together (see text).

[b] The abundances of the deuterated species CH_3OHD^+ and $CH_2DOH_2^+$ are added together (see text).

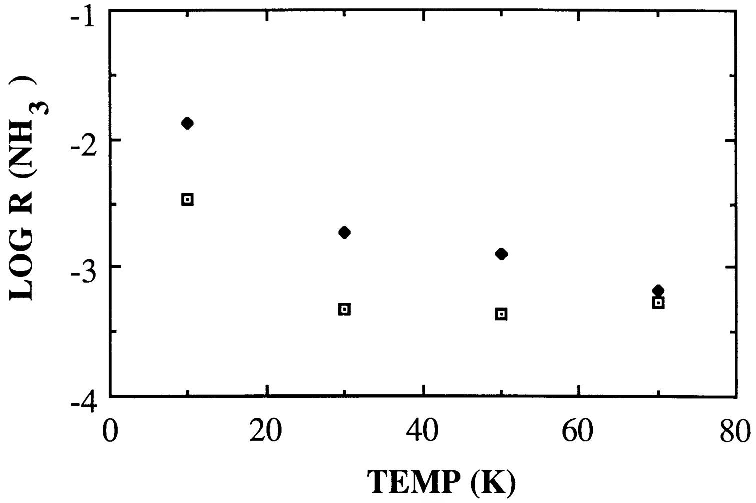

FIG. 3.—Logarithm of the calculated abundance ratio $R(NH_3) = [NH_2D]/[NH_3]$ plotted against temperature at early time. *Diamonds:* values obtained with the new dissociative recombination branching ratios; *open squares:* values obtained with the old dissociative recombination branching ratios.

ratios are presented for models using the "new" branching ratios. Figure 1 shows $R(HCO^+)$ and $R(H_3^+)$ as functions of time for a warm ($T = 70$ K) cloud, while Figures 3–6 give R at early time as a function of temperature for selected species. These and other results will be discussed in the following section. Unless otherwise specified, our discussion will be limited to those calculations in which the old dissociative recombination branching ratios have been utilized.

IV. DISCUSSION

Deuterium in dense interstellar clouds can be fractionated into molecules via reactions involving the three "basic" deuterated ions and their derivatives. These three ions—H_2D^+, CH_2D^+, and C_2HD^+—are enriched in deuterium directly via reaction with HD (see Table 1) in reactions (4), (7), and (8), respectively. As a consequence of these reactions, subsequent fractionation of other species occurs. At $T = 10$ K, $R(H_3^+) \approx$ 0.11–0.16, and deuteron transfer reactions from H_2D^+ are important in the formation of most deuterated species at all times. These species include ions such as DCO^+ and H_2DO^+ as well as neutrals. Deuteration of neutrals also proceeds through these latter two ions. As the temperature is increased from 10 to 70 K, however, H_2D^+ is increasingly destroyed by H_2 since the endothermic reaction in formula (4) achieves an appreciable rate coefficient, and the fractionation falls appreciably. Fractionation via D atoms derived from DCO^+ also falls strongly with increasing temperature, especially at steady state.

Reactions (7) and (8) cause efficient fractionation of neutral hydrocarbon molecules such as CH_4, CCH, C_2H_3, and other species such as H_2CO, CH_2CO, and CH_3OH, which are formed via reactions involving hydrocarbons ions and/or neutrals. Because of the large enthalpies of reactions (7) and (8), fractionation is efficient at all times, even at 70 K, with R(CCH) and $R(H_2CO) \approx 0.01$–0.02 and the deuterium abundance ratios of selected other hydrocarbons and hydrocarbon-related species even greater. These values are much larger at 70 K than that of a species which derives its fractionation from H_2D^+, e.g., $R(N_2H^+) \approx (0.75$–$3.8) \times 10^{-4}$.

In the remainder of this section we discuss our results in some detail. Readers uninterested in this detail can profitably

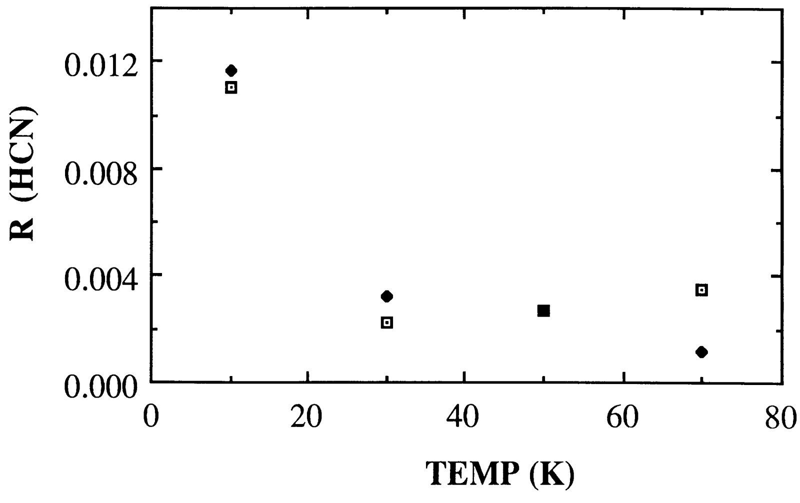

FIG. 4.—Calculated abundance ratio R(HCN) plotted against temperature at early time. The diamonds and squares have the same meaning as in Fig. 3.

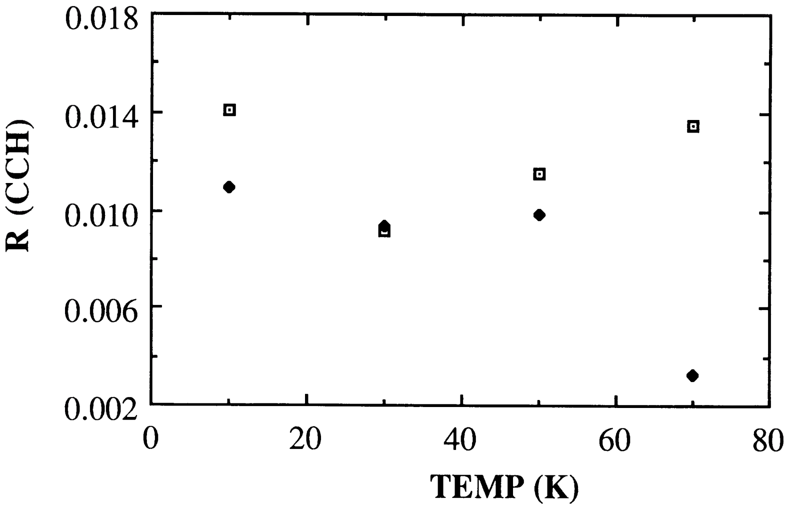

FIG. 5.—Calculated abundance ratio R(CCH) plotted against temperature at early time. The diamonds and squares have the same meaning as in Fig. 3. Note the sharp discrepancy between the two sets of points at 70 K.

skip to § V, in which our results are compared with observation.

a) Time Dependence

In general, the degree of deuterium fractionation in many molecules is only slightly dependent on time in the range 3×10^5–10^8 yr, with variations of less than a factor of 4, especially at the lower temperatures. This behavior contrasts with the behavior of the absolute abundances during the interval of time, which can vary by several orders of magnitude. One species for which time dependence is significant is DCO^+. The time dependence of this species shows up particularly for $T \geq 30$ K when reactions other than those involving H_2D^+ affect the degree of fractionation. Figure 1 shows $R(H_3^+)$ and $R(HCO^+)$ calculated for $T = 70$ K. As expected, $R(H_3^+)$ is small (2×10^{-4}), but, surprisingly, $R(HCO^+)$ is very large at early times, reaching a maximum value of 0.006 at 3.2×10^4 yr, and remaining large ($R = 0.003$) at "early time" (3.2×10^5 yr). Obviously, this large ratio at early times cannot be due to the reaction

$$H_2D^+ + CO \rightarrow DCO^+ + H_2 , \qquad (13)$$

which is normally considered to be the mechanism capable of fractionating DCO^+. At early times, DCO^+ is formed predominantly through the reaction

$$CH_4D^+ + CO \rightarrow DCO^+ + CH_4 , \qquad (14)$$

since the CH_4D^+ species is fractionated at high temperatures to a far greater extent than is H_2D^+ and, like all hydrocarbons, is much more abundant at early times than at steady state. In addition to this reaction, there are significant contributions to DCO^+ formation in the reactions

$$C_2HD^+ + O \rightarrow DCO^+ + CH \qquad (15)$$

and

$$CD + O \rightarrow DCO^+ + e . \qquad (16)$$

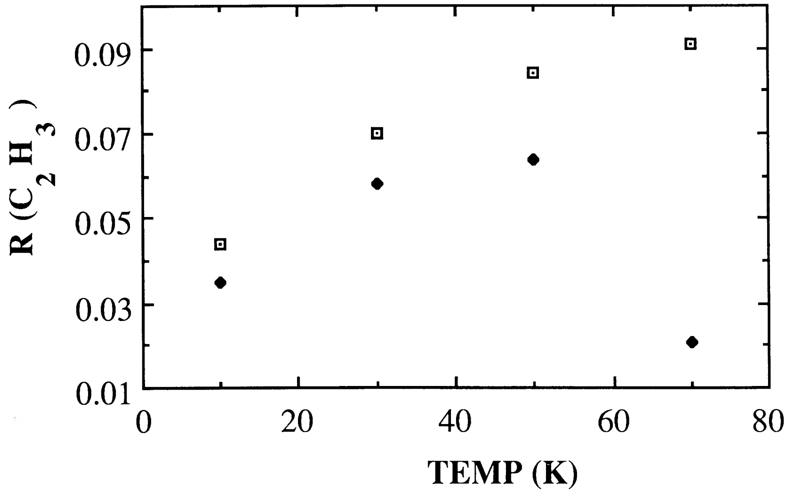

FIG. 6.—Calculated abundance ratio $R(C_2H_3)$ plotted against temperature at early time. The diamonds and squares have the same meaning as in Fig. 3. Note the sharp discrepancy between the two sets of points at 70 K.

since both C_2HD^+ and CD are fractionated to a considerable degree at 70 K. The time-dependent behavior of $R(HCO^+)$ may help explain the DCO^+ observations in Orion, as will be discussed in § V.

For neutral species fractionated by both H_2D^+ and DCO^+, there is a significant difference at 70 K, and to a lesser extent at 50 K, between early-time and steady state values of R owing to the large abundance of DCO^+ at early time.

b) *Temperature Dependence and Propagation of Deuteration*

The temperature dependence of the deuterium fractionation for a given species is determined by the mechanism of fractionation—whether it proceeds directly or indirectly from H_2D^+, on the one hand, or from the deuterated hydrocarbon ions—CH_2D^+ and C_2HD^+, on the other hand.

i) *Species Fractionated by* H_2D^+

Any neutral molecule which has a deuteron affinity greater than H_2 will be enriched in deuterium as a result of reaction with H_2D^+, with one-third of the collisions leading to the transfer of a deuteron. With the additional assumption that the normal and deuterated ion are depleted at exactly the same rate, this factor of $\frac{1}{3}$ should be seen in the abundance ratios R for ions formed principally from H_2D^+. Indeed, this factor can be seen in Table 2 for ions such as N_2D^+, H_2DO^+, and DCO^+ (at steady state); the difference from the exact value of $\frac{1}{3}$ occurs because of secondary fractionation mechanisms and differences in depletion rates. Neutral molecules which result from the recombination of ions such as these are more complicated. Their deuteration ratios result from a complex interplay involving the extent of fractionation preserved in dissociative recombination reactions and the overall loss rate for the deuterated neutral species via ion-molecule reactions. (See the discussion concerning NH_2D in § IV*c* below.)

Because of the relatively small enthalpy change in reaction (4), destruction of H_2D^+ is dominated by H_2 once the temperature exceeds 30 K, and fractionation via H_2D^+ becomes unimportant. This is clear from Table 2, particularly at steady state when fractionation by DCO^+ is unimportant, and is shown for NH_3, which derives its fractionation from H_2D^+ and descendant ions, in Figure 3. This figure shows $R(NH_3)$ at early time as a function of temperature for both old and new dissociative recombination branching ratios. The decrease with increasing temperature for $R(NH_3)$ is particularly evident for the new branching ratios.

The deuterated ion DCO^+ leads to D atom formation via dissociative recombination reactions (Dalgarno and Lepp 1984). D atoms lead to a huge fractionation for the radical OH at steady state when $T = 10$ K with $R(OH) = 0.59$! The OH molecule is deuterated by the reaction (Croswell and Dalgarno 1985)

$$D + OH \rightarrow OD + H , \tag{17}$$

and the OD so formed is destroyed by

$$O + OD \rightarrow O_2 + D . \tag{18}$$

Hence,

$$R(OH) = k_{17}[D]/k_{18}[O] . \tag{19}$$

At 10 K, $k_{17} = 1.3 \times 10^{-10}$ cm^3 s^{-1} (Croswell and Dalgarno 1985), $k_{18} = 7.3 \times 10^{-12}$ cm^3 s^{-1}, and (at steady state) $[D] = 1.4 \times 10^{-6}$ and $[O] = 4 \times 10^{-5}$, giving the exceptionally large value for $R(OH)$. This large value decreases precipitously as temperature increases, however, since the D atom abundance falls. $R(OH)$ is still significant at early time at $T = 70$ K, since DCO^+ is higher at early time than at steady state. As suggested by Croswell and Dalgarno (1985), OD should be searched for in interstellar clouds.

ii) *Species Fractionated by* CH_2D^+

Reaction (7) leads to deuterium enhancement in CH_2D^+ which, because of the enthalpy change of -370 K (Smith, Adams, and Alge 1982*a*, *b*), is efficient at higher temperatures than reaction (4). Because CH_2D^+ has a relatively rapid radiative association reaction with H_2 (reaction [9]) the reverse reaction in formula (7) does not dominate the destruction of CH_2D^+ until $T \geq 70$ K. Hence reaction (9), which preserves the deuterium in a hydrocarbon ion, is crucial in extending the ability of reaction (7) to fractionate at high temperatures. Further, since the rate coefficient of reaction (9) is estimated to have a $T^{-0.5}$ dependence, the degree of fractionation in CH_3^+ should vary as $T^{0.5}$. This behavior is clearly noticeable in Table 2 in the range $30 \leq T \leq 70$ K. At 10 K, $R(CH_3^+)$ is higher than anticipated because of a series of reactions starting with $C + H_2D^+$. Above 70 K, $R(CH_3^+)$ decreases strongly as a result of the endothermic exchange reaction between CH_2D^+ and H_2.

The fractionation in CH_2D^+ can be transferred to other molecules. Examples of species formed directly from this ion are CHDCO (deuterated ketene) and CH_2DCN (deuterated acetonitrile). These are formed via the radiative association reactions

$$CH_2D^+ + CO \rightarrow CH_2DCO^+ + h\nu , \tag{20}$$

$$CH_2D^+ + HCN \rightarrow CH_2DCNH^+ + h\nu , \tag{21}$$

followed by dissociative recombination. The species HDCO (deuterated formaldehyde) is formed from two species derived from CH_2D^+—CH_4D^+ and CH_2D—via the reactions

$$O + CH_4D^+ \rightarrow H_2DCO^+ + H_2 , \tag{22}$$

followed by dissociative recombination, and

$$O + CH_2D \rightarrow HDCO + H . \tag{23}$$

Even at 70 K, $R(H_2CO) \approx 0.01$–0.02. Another species formed from a derivative of CH_2D^+ is DCN, which derives mainly from the neutral-neutral reaction

$$N + CHD \rightarrow DCN + H . \tag{24}$$

This reaction, in analogy to suggestions concerning the $N + CH_2$ reaction, has an activation energy of ≈ 50 K if one assumes a negligible kinetic isotope effect. If so, it does not contribute to DCN formation at $T < 30$ K, at which temperatures fractionation via H_2D^+ and DCO^+ dominates, but it does become more efficient at higher temperatures and causes $R(HCN)$ to increase with temperature in the models with the old branching ratios for $T \geq 30$ K, as shown in Figure 4. We also note that at high temperatures $R(H_2CO) > R(HCN)$ by up to an order of magnitude because the most fractionated deuterium-bearing ion in the CH_nD^+ chain is CH_4D^+, a precursor of HDCO, whereas DCN derives from CHD, which comes from CH_2D^+.

Finally, it should be remembered that at early time the unusually large abundance of DCO^+ at high temperatures stems from CH_4D^+ (see reaction [14]). Since DCO^+ subsequently leads to fractionation of a wide variety of neutrals, the relatively large R-values for these species ($R \approx 10^{-3}$) at early time and high temperature can be ascribed indirectly to CH_2D^+ through reaction (9).

iii) *Species Fractionated by* C_2HD^+

Reaction (8) has the largest enthalpy change of the three major HD–molecular ion fractionation reactions in our model. Therefore, fractionation via C_2HD^+ is efficient at still higher temperatures than fractionation via CH_2D^+ and causes fractionation in CCD and higher hydrocarbon species. Loss of C_2HD^+ is dominated by radiative association with H_2 at temperatures under 70 K:

$$C_2HD^+ + H_2 \rightarrow C_2H_3D^+ + h\nu \,, \qquad (25)$$

just as is the case for CH_2D^+, rather than via the endothermic exchange reaction with H_2. At low temperatures, therefore, we expect that

$$R(C_2H_2^+) \approx (k_{8f}[HD])/(k_{25}[H_2]) \,, \qquad (26)$$

where k_{8f} refers to the forward rate coefficient in reaction (8). Equation (26) leads to a predicted value for R of ≈ 0.05 at 10 K. Although this relationship holds at early time, $R(C_2H_2^+)$ is larger than predicted at steady state because C_2HD^+ is also produced by the reaction

$$C^+ + CH_3D \rightarrow C_2HD^+ + H_2 \,, \qquad (27)$$

as well as from reactions involving H_2D^+ and DCO^+ with CCH. Because of the efficiency of reaction (25), much of the effect of fractionation in C_2HD^+ is transferred to $C_2H_3D^+$. Dissociative recombination of this ion leads to the large values of $R(C_2H_2)$ and $R(C_2H_3)$ calculated at 10 K.

As the temperature increases, the rate coefficient of reaction (25) decreases, $R(C_2H_2^+)$ increases, and dissociative recombination of C_2HD^+ to form CCD + H becomes more competitive. This reaction and the route to CCD through CH_3D cause R(CCH) to increase with increasing temperature for $T > 30$ K when the old branching ratios are utilized. Such behavior (shown in Fig. 5) was predicted by Herbst *et al.* (1987).

The increase in $R(C_2H_2^+)$ with increasing temperature leads to an increase in $R(C_2H_4^+)$ because $C_2H_3D^+$ and $C_2H_4^+$ derive mainly from C_2HD^+ and $C_2H_2^+$, respectively, via radiative association reactions. Figure 6 shows that $R(C_2H_3)$ increases with increasing temperature over the full range 10–70 K for the old dissociative recombination branching ratios. This behavior reflects the temperature dependence of $R(C_2H_4^+)$, since $C_2H_3D^+$ is a precursor to C_2H_2D.

Reactions of C^+ with C_2H_2D transfer fractionation to the C_3-bearing hydrocarbons via

$$C^+ + C_2H_2D \rightarrow C_3HD^+ + H \,, \qquad (28)$$

and subsequently to C_3D via dissociative recombination. Such fractionation is not transferred easily to the more hydrogen-rich C_3 hydrocarbons, such as C_3H_2, since C_3HD^+ cannot be further hydrogenated. Rather, fractionation in C_3H_2 is related to that in C_2H_2 through the reactions (Bell *et al.* 1988)

$$C^+ + C_2HD \rightarrow C_3D^+ + H \,, \qquad (29)$$

$$C_3D^+ + H_2 \rightarrow C_3H_2D^+ + h\nu \,, \qquad (30)$$

$$C_3H_2D^+ + e \rightarrow C_3HD + H \,. \qquad (31)$$

It is of interest to show how isotopic fractionation is lost to some degree as it propagates. It can be shown that the expected fractionation in C_3H_2 based on the above reactions should be given by the approximate formula

$$R(C_3H_2) \approx \{0.5f(1-f')/[f'(1-f)]\}R(C_2H_2) \,, \qquad (32)$$

where f and f' are the branching ratios leading to C_3HD and C_3H_2, respectively, in the dissociative recombination reactions involving $C_3H_2D^+$ and $C_3H_3^+$, and where it has been assumed that depletion of the neutral species occurs primarily through reactions with protonating ions such as H_3^+. With $f' = 0.5$ (old view of branching ratios) and $f = \frac{2}{3}f'$ (statistical view), we obtain $R(C_3H_2) \approx 0.25R(C_2H_2)$. Except for 10 K, when deuteration via H_2D^+ and DCO^+ is important, this relationship holds approximately at steady state, as can be seen from Table 2. At early time, the influence of DCO^+ changes this relationship. For early time, $R(C_3H_2) \geq 0.01$ at all temperatures up to 70 K, and C_3HD might therefore be detectable in warm sources as are CCD and HDCO.

c) *Branching Ratio Dependence*

Table 3 presents our results when the new dissociative recombination branching ratios are utilized (Millar *et al.* 1988). The differences between these results and those in Table 2 are due to a number of effects. For species which are deuterated via H_2D^+ and/or descendant ions, fractionation is typically less at low temperatures when the new branching ratios are used because of the increased abundance of H_2O which results because all dissociative recombinations of H_3O^+ lead to H_2O (Bates 1986*a*, 1987*a*) and because of an increase in the O abundance (Millar *et al.* 1988). The H_2D^+ ion reacts with both H_2O and O, and its abundance relative to H_3^+ is reduced by a factor of about 3.5 at steady state and a temperature of 10 K. At higher temperatures, loss of H_2D^+ occurs predominantly via reaction with H_2 and $R(H_3^+)$ is essentially independent of the mode of recombination. It is of course true that some of the decrease in H_2D^+ at low temperatures when the new branching ratios are used is compensated for by an increase in the abundance of the H_2DO^+ ion, formed via the reaction of H_2D^+ and H_2O. However, the H_2DO^+ ion does not undergo exothermic deuteron transfer to as many species as does H_2D^+.

Somewhat surprisingly, $R(NH_3)$ is increased significantly when the new branching ratios are used (Fig. 3), especially at low temperatures. Ammonia is deuterated at low temperatures by H_2D^+ with the old branching ratios and by H_2DO^+ with the new ratios. In both cases deuteration by DCO^+ also occurs. For H_2D^+ and H_2DO^+, the initial deuteration proceeds at one-third of the rate of reaction between ammonia and the deuterated ion. Once NH_3D^+ is formed, it dissociatively recombines with electrons to form a variety of products. If one labels $0.75f$ the branching ratio leading to $NH_2D + H$ and $0.25f$ the branching ratio leading to $NH_3 + D$, one obtains the following equation for $R(NH_3)$:

$$R(NH_3) = [0.25f/(1-0.75f)]y \,, \qquad (33)$$

where

$$y = \{k_a[H_2D^+] + k_b[H_2DO^+] + 3k_c[DCO^+]\} \times \{k_a[H_3^+] + k_b[H_3O^+] + k_c[HCO^+]\}^{-1} \,, \qquad (34)$$

with the additional assumption that depletion of NH_2D proceeds mainly via protonation with H_3^+, HCO^+, or H_3O^+ and that a statistical fraction of the newly protonated NH_3D^+ finds its way back into NH_2D. The rate coefficients in equation (34) refer to reactions of NH_3 with the assorted ions. For the new branching ratios $f = 1$, whereas for the old $f = \frac{1}{4}$. Then we predict from this simple analysis that $R(\mathrm{NH_3}) = y$ and $R(\mathrm{NH_3}) = y/13$ for the two cases, respectively, a prediction in reasonable if not perfect agreement with our detailed results. Thus, even though y is somewhat lower for the new branching ratios, the factor of 13 renders $R(\mathrm{NH_3})$ higher. Note that, for other species, unlike the case of $\mathrm{NH_4^+}$, f is normally smaller with the new branching ratios, since more exit channels are open.

For most species deuterated by other mechanisms such as hydrocarbons, use of the new branching ratios causes somewhat of a decrease in the fractionation, particularly at high temperatures, as shown for R(CCH) in Figure 5. At the lower temperatures the decline is caused by the larger number of product channels available in dissociative recombination reactions. The reason for the sharp decrease at 70 K is especially complex and highlights the need for detailed model calculations. The decrease occurs because the new branching ratios result in a larger C I abundance (by ≈ 10 at early time and $\approx 10^3$ at steady state at a temperature of 70 K). This in turn occurs because little OH and hence little O_2 are formed with the new branching ratios and because O_2 is normally the most important destruction mechanism for C I (Millar *et al.* 1988). As a result, the reactions between C I and the $\mathrm{CH_nD^+}$ hydrocarbons become more important in forming $\mathrm{C_2HD^+}$ and $\mathrm{C_2H_2D^+}$, which recombine to CCD, while at the same time C I reactions with these latter ions transfer the deuteration into the higher hydrocarbon ions. The net result is that CCD reflects the behavior of the $\mathrm{CH_nD^+}$ ions, which, because the enthalpy change in reaction (7) is smaller than in reaction (8), have a reduced fractionation at 70 K.

V. COMPARISON WITH OBSERVATION

The abundances of nine deuterated molecules have been determined for the cold ($T = 10$ K) cloud TMC-1 and an upper limit determined from the nondetection of $\mathrm{NH_2D}$. The observed abundance ratios are listed in Table 4, although we note that some ratios are uncertain because of large optical depths or self-absorption in the nondeuterated species. In Table 4 we also give the range of ratios obtained from our $T = 10$ K models for both old and new dissociative recombination branching ratios. The theoretical results are given in the form "early-time ratio–steady state ratio." On the basis of these results, it appears that the early-time results give a slightly better fit to the observed abundance ratios when the old dissociative recombination branching ratios are utilized. With the new values, there is little difference between the early-time and the steady state results. Agreement between calculated and observed values is encouraging in all cases. Of course, in an absolute sense, early-time abundances are in much better agreement with observation for all complex molecules in models of this type. One notable failure of the theoretical models is in describing the fractionation in $\mathrm{C_3HD}$, which is roughly an order of magnitude larger than those of most other molecules in TMC-1 (Bell *et al.* 1988). It is difficult to see how such a large ratio can arise unless some mechanism such as the Gellene-Porter process (§ II) is at work (Bell *et al.* 1988) or there is a path from the highly fractionated $\mathrm{C_2H_3}$. However, in normal ion-molecule schemes, the $\mathrm{C_2H_3}$ radical is not a precursor of $\mathrm{C_3H_2}$ (see the discussion in § IV*b*). If the Gellene-Porter mechanism is at work, why is the fractionation in CCD so much lower than in $\mathrm{C_3HD}$?

One possible mechanism for increasing the fractionation of complex molecules at low temperatures is to use a smaller rate coefficient for the $\mathrm{CH_3^+} + \mathrm{H_2} \rightarrow \mathrm{CH_5^+} + h\nu$ radiative association, which would boost the concentration of $\mathrm{CH_3^+}$ and, by reaction (7), $\mathrm{CH_2D^+}$. We have therefore run models at $T = 10$ K with the value of this rate coefficient at the low value given by Herbst (1985). At early time, $R(\mathrm{C_3H_2})$ does increase, but only by a factor of 1.5. The increased value of R is still much less than that observed in TMC-1, while R(CCH) increases by ≈ 2 and is more discrepant with observation.

Table 5 presents the observed deuterium abundance ratios for a warm source, Orion, and compares these with the results of our $T = 70$ K models. This temperature is close to that derived for Orion from both $\mathrm{SO_2}$ (Pickett and Davis 1979) and CO (Richardson *et al.* 1985) observations. In Orion there are only five deuterated species detected in the ambient cloud ("extended ridge"): $\mathrm{DCO^+}$, DCN, DNC, CCD, and HDCO. Three other species, $\mathrm{NH_2D}$, $\mathrm{CH_3OD}$, and HDO, have been

TABLE 4

DEUTERIUM ABUNDANCE RATIOS IN TMC-1 COMPARED WITH THEORETICAL VALUES AT 10 K

		R (calculated)		
SPECIES	R (observed)	"Old"	"New"	REFERENCES
$\mathrm{HCO^+}$	0.015 ± 0.002	0.031–0.054	0.019–0.018	GLW
$\mathrm{N_2H^+}$	0.045[a]	0.033–0.049	0.021–0.016	GLW
HCN	0.023 ± 0.001	0.011–0.043	0.012–0.022	W
HNC	0.015	0.018–0.018	0.019–0.023	GLW
CCH	0.01	0.014–0.034	0.011–0.011	F
$\mathrm{C_3H_2}$	0.08–0.16	0.012–0.032	0.010–0.013	B
$\mathrm{H_2CO}$	0.005–0.11[b]	0.032–0.064	0.024–0.033	L, GLW
$\mathrm{HC_3N}$	0.015 ± 0.005	0.019–0.049	0.009–0.009	S
$\mathrm{HC_5N}$	0.013 ± 0.004[c]	0.020–0.039	0.013–0.013	MAB, SSLY
$\mathrm{NH_3}$	<0.02	0.003–0.015	0.013–0.100	O

NOTE.—For calculated values the early-time result precedes the steady state result.

[a] Upper limit only—$\mathrm{N_2H^+}$ is self-absorbed.

[b] Large range because $\mathrm{H_2CO}$ abundance is uncertain. GLW estimate 0.015.

[c] Average value from two measurements.

REFERENCES.—GLW: Guélin, Langer, and Wilson 1982; W: Wootten 1987; F: Friberg 1986, private communication; B: Bell *et al.* 1988; L: Langer *et al.* 1979; S: Suzuki 1987; MAB: MacLeod, Avery, and Broten 1981; SSLY: Schloerb *et al.* 1981; O: Olberg *et al.* 1985.

TABLE 5

Deuterium Abundance Ratios in Orion Compared with Theoretical Values at 70 K

		R (calculated)		
Species	R (observed)	"Old"	"New"	References
HCO^+	0.002	0.003–1(−4)	8(−4)–8(−5)	P
HCN	0.006 ± 0.001	0.004–0.001	0.001–4(−4)	W
HNC	0.01	0.003–1(−4)	9(−4)–2(−4)	BR81
CCH	0.045	0.014–0.016	0.003–0.003	C, V
H_2CO	0.02 ± 0.01	0.019–0.012	0.004–0.005	LW
NH_3	0.003[a]	6(−4)–7(−5)	4(−4)–2(−4)	WH
CH_3OH	0.01–0.06[a]	0.011–0.002	0.003–0.004	M
H_2O	>0.002[a]	0.002–7(−5)	0.001–2(−4)	H

Note.—Calculated abundances listed as $a(-b)$ refer to $a \times 10^{-b}$. Calculated early-time values precede steady state values.

[a] Ratios observed toward Orion-KL and not indicative of the ambient gas.

References.—P: Penzias 1979; W: Wootten 1987; BR81: Brown and Rice 1981; C: Combes *et al.* 1985; V: Vrtilek *et al.* 1985; LW: Loren and Wootten 1985; WH: Walmsley *et al.* 1987; M: Mauersberger *et al.* 1988; H: Henkel *et al.* 1987.

detected in the "hot core" and/or "compact ridge" regions, which have a kinetic temperature of 100–150 K (Menten *et al.* 1988; Walmsley *et al.* 1987; Henkel *et al.* 1987; Mauersberger *et al.* 1988).

For the species in the ambient cloud, it is clear that theory and observation are in reasonable agreement at early time if the old branching ratios are utilized. At steady state there is a strong disagreement between theory and observation for HCO^+, with the theoretical value being too low by more than an order of magnitude. A similar disagreement occurs for HNC and, to a lesser extent, HCN. The theoretically determined abundance ratios obtained using the new branching ratios are generally much too low at both early time and steady state.

Wootten (1987) has discussed the observed values of R(HCN) in a variety of sources at differing temperatures. His plot of R(HCN) versus temperature, which indicates little temperature dependence for $T > 20$ K, is in excellent agreement with our calculated early-time values shown in Figure 4, especially if the old dissociative recombination branching ratios are used.

For the "hot core" and "compact ridge" species in Orion, the results in Table 5 show that our theoretical results at 70 K are less to much less than the observed ratios, a discrepancy which will be exacerbated at the still higher temperatures which pertain to these sources. Since the absolute abundances of NH_3 and CH_3OH are much larger than their abundances in cold dense clouds, it is likely that some processes other than ambient gas-phase chemistry such as grain desorption (Mauersberger *et al.* 1988 and references therein) are needed to understand the observations. Brown, Charnley, and Millar (1988) have recently developed a model of the "hot core" region which incorporates grain surface processing and which reproduces the observed abundances successfully. An extension of this model to include "deuterium chemistry" has been undertaken (Brown and Millar 1989). We note that the observed deuteration abundance ratios are in reasonable agreement with our theoretical results at temperatures in the vicinity of ≈20 K, a temperature that has been derived based on differences in abundance between the A and E torsional substates of ^{13}C methanol by Menten *et al.* (1988). This low temperature may reflect a previous low-temperature phase for the material (Brown, Charnley, and Millar 1988).

VI. COMPARISON WITH RESULTS OF BROWN AND RICE

Differences between our results and those of Brown and Rice (1986, hereafter BR) stem from a variety of factors, some of which (e.g., choice of initial concentrations, choice of elemental abundances) are unrelated to the deuterium chemistry. These factors are minimized by comparison of their steady state, "low metal" results with ours obtained using the "old" dissociative recombination branching ratios. Both models contain the same density and range of temperatures. In most of the comparisons discussed below, we have read the BR results from figures.

The two major factors that lead to differences between our results and those of BR are as follows: (1) the contrasting treatments of the temperature dependence of k_r in reaction (4), and (2) the inclusion or exclusion of the radiative association reactions with H_2 that deplete the important ions CH_2D^+ and C_2HD^+. These factors are discussed separately.

The rate coefficient k_r for the endothermic reaction between H_2D^+ and H_2 is best calculated by considering the temperature dependence of the entropy and enthalpy terms via the use of partition functions (Herbst 1982). The results of such a calculation are shown here in Table 1. BR instead used the simple formula $k_r = 1.7 \times 10^{-9} \exp(-B/T)$ (cm^3 s^{-1}) with two values for B—150 and 230 K—and asserted (correctly) that the true values of k_r as a function of temperature lie in between their values of k_r computed with the two limiting numbers for B. However, use of the two numbers for B leads to widely divergent limits for k_r. For example, at 30 K, BR calculate that $k_r = 8.0 \times 10^{-13}$ cm^3 s^{-1} if $B = 230$ K, and $k_r = 1.1 \times 10^{-11}$ cm^3 s^{-1} if $B = 150$ K, a difference of over an order of magnitude. At intermediate temperatures in the 10–70 K range, when the size of k_r is critical, this range of possible values leads to a large range in their calculated results for $R(H_3^+)$. For example, at 30 K, they calculate that $R(H_3^+)$ can be anywhere in the range from 4×10^{-3} to 4×10^{-2}. Our computed value for k_r at 30 K is much closer to the BR result obtained when $B = 150$ K and leads to $R(H_3^+) = 4.9 \times 10^{-3}$. At lower temperatures ($T \approx 10$ K), the value of k_r is sufficiently small when calculated correctly or with either number for B that the reaction between H_2D^+ and H_2 is unimportant and the BR value for $R(H_3^+)$ is in close agreement with ours. At the high temperature of 70 K, k_r is rather large no matter how it is calculated, so that the fractionation is minimal and the discrepancy between us and BR not very large. Thus, the worst disagreement (almost an order of magnitude) occurs at intermediate temperatures if $B = 230$ K is chosen. The disagreement in $R(H_3^+)$ leads to disagreements in many other species deuterated by H_2D^+ either directly or indirectly. For example, at 30 K, we compute that $R(HCO^+) = 2.1 \times 10^{-3}$, which is smaller than the $B = 230$ K BR result by over an order of magnitude (depending also on whether atomic deuterium processes are included) but is in good agreement with the $B = 150$ K BR value.

The role of the radiative association reactions in our model is clearly a critical one in the determination of the temperature dependence of the deuterium fractionation for carbon-containing species. Having preceded the papers on this subject by Herbst *et al.* (1987) and Wootten (1987), BR did not include this important effect. The result is that for organic species we predict a smaller dropoff of fractionating effects as temperature is increased or indeed, in the limited 10–70 K temperature range, an actual increase in fractionation as temperature is increased. Consider two molecules for which BR provide diagrams of fractionation versus temperature. BR calculate that $R(CH_3^+)$ decreases as temperature increases from 10 to 70 K by a factor of 10–30, whereas in our model $R(CH_3^+)$ actually increases, albeit slightly! BR also calculate that R(HCN) decreases strongly with increasing temperature above 30 K [$R(30 \text{ K}) \approx 10^{-2.0}$ to $10^{-2.5}$; $R(70 \text{ K}) \approx 10^{-3.0}$ to $10^{-3.5}$), whereas in our model R(HCN) is fairly independent of temperature in this range.

In addition to these two major and widespread factors, another factor causing disagreement between the two models is the lack of inclusion in BR of the Croswell and Dalgarno (1985) mechanism for fractionation of OH by deuterium atoms (reaction [17]). At 10 K we calculate R(OH) to be near unity, whereas they calculate it to be $10^{-1.9}$.

Interestingly, one factor that should not cause much disagreement is the uncertain rate of the H_3^+ and H_2D^+ dissociative recombination reactions with electrons (Adams, Smith, and Alge 1984; Amano 1988), since these ions are depleted more rapidly via reaction with carbon monoxide even if the largest possible dissociative recombination rate coefficients are utilized.

VII. CONCLUSIONS

Our detailed numerical model of deuterium fractionation in dense interstellar clouds has shown that a variety of primary and secondary processes can contribute to the deuteration of interstellar molecules and that for most species it is necessary to calculate deuterium fractionation ratios numerically rather than by considering only a few reactions at steady state. However, certain trends are apparent. At low temperatures, fractionation is caused mainly by reactions involving H_2D^+ and associated ions (DCO^+, H_2DO^+) which derive ultimately from H_2D^+. Other fractionation mechanisms are important but are not as global in scope. As the temperature increases, fractionation caused by H_2D^+ diminishes rapidly, while fractionation caused by CH_2D^+ and C_2HD^+ and dependent species (including DCO^+ at early time) remains effective, even increasing with increasing temperature for selected species. This unusual temperature dependence comes from the fact that the rate-determining depletion reactions of CH_2D^+ and C_2HD^+ are radiative association reactions with H_2 that possess rate coefficients with an inverse dependence on temperature (Herbst *et al.* 1987). Fractionation via the hydrocarbon ions results in large deuterium abundance ratios at temperatures as high as 70 K for hydrocarbons and species such as H_2CO which derive their fractionation from precursor hydrocarbons.

The deuterium abundance ratios calculated at 10 K are consistent with those observed in TMC-1 for most species, whether one considers early-time or steady state results (although absolute abundances are in agreement only at early time) and whether or not one uses the new or the old dissociative recombination branching ratios. Comparison between theory and observation for Orion, however, indicates that, for species in the ambient molecular cloud, the early-time results obtained with the old dissociative recombination branching ratios are superior if a temperature of 70 K is utilized. For those species located in the "hot core" and/or "compact ridge" regions of the Orion source, our high-temperature results are not in good agreement with observation. It is likely that the high deuterium fractionation abundances found in these regions are due to an earlier low-temperature phase.

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Note added in proof.—Recent preliminary experiments by Smith and Adams (Birmingham, United Kingdom, private communication) show that for the dissociative recombination reaction between H_3O^+ and electrons, the OH product channel dominates. The "new" dissociative recombination branching ratios used in this paper are therefore in error in neglecting channels in which an H_2 molecule or two H atoms are produced.

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