

Kinetic Isotopic Fractionation and the Origin of HDO and CH₃D in the Solar System¹

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Received May 18, 1987; revised November 15, 1987

It is argued that photochemical processes, driven by ultraviolet starlight, could lead to large deuterium fractionation for H₂O and CH₄ relative to H₂ in the primitive solar nebula. Implications for deuterium enrichment observed in planetary atmospheres are briefly discussed. © 1988 Academic Press, Inc.

1. INTRODUCTION

The deuterated species that have been measured in the Solar System exhibit considerable isotopic variation (Geiss and Reeves 1981, Gautier and Owen 1983). We now understand that there is a large deuterium enrichment, relative to the Jovian planets, in the volatiles present in the atmospheres of the terrestrial planets (Craig

and Lupton 1976, Donahue *et al.* 1982, McElroy *et al.* 1982, Owen *et al.* 1987) and in the atmospheres of Titan and Uranus (Kim and Caldwell 1982, Owen *et al.* 1986, Pinto *et al.* 1986, de Bergh *et al.* 1986). The D/H ratio in the cometary atmosphere of Halley (Eberhardt *et al.* 1986) is enhanced by factors 4–30 (relative to Jupiter), and even larger enrichment factors have been reported for the organic components of carbonaceous meteorites (Kerridge 1982, Robert and Epstein 1982, Becker and Epstein 1982, Yang and Epstein 1983).

The classical explanation of isotopic enrichment in the solar nebula is based on the fact that equilibrium partitioning of deute-

¹ Presented at the Conference on Origin and Evolution of Planetary and Satellite Atmospheres, March 10–14, 1987, Tucson, AZ. Contribution No. 4454 from the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

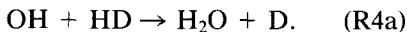
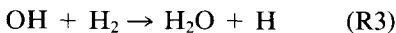
rium between molecular species at low temperatures could lead to substantial fractionation for H₂O, CH₄, and NH₃ in a larger reservoir of H₂ (Richet *et al.* 1977, Hubbard and MacFarlane 1980). However, the time for reaching thermochemical equilibrium (even with catalysis on the surface of metal rich grains) at low temperatures is too long compared with the lifetime of the nebula (Grinspoon and Lewis 1987). In this article we propose an alternative mechanism, based on photochemistry, that can produce similar effects in a much shorter time. This work is highly speculative and is partly motivated by recent attempts to seek a kinetic explanation for the enrichment of the ¹⁸O/¹⁶O ratio observed in meteorites (Thiemens and Heidenreich 1983, Kitamura and Shimizu 1984, Navon and Wasserburg 1985).

2. PHOTOCHEMISTRY

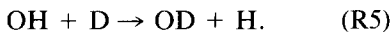
Consider the photolysis of H₂O in the solar nebula initiated by the absorption of ultraviolet radiation at wavelengths <1975 Å (see, for example, Allen *et al.* 1981),



(see Table I for the numbering of chemical reactions). In this work we shall be concerned primarily with the continuum interstellar radiation field. Line sources, such as Ly α and He 584 Å, may provide additional contributions (Strobel *et al.* 1980), but probably would not change the order of magnitude of our estimated interstellar field. The most likely fate of OH is to react with H₂ and HD,



The net result is the photosensitized dissociation of H₂ and HD with H₂O playing the role of a catalyst. The presence of OH and D in the solar nebula leads to rapid isotopic exchange between the radicals,



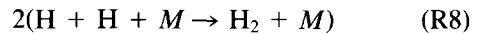
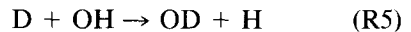
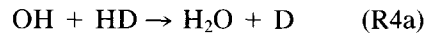
OD is removed by reaction with H₂, yielding HDO,



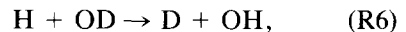
The H atoms produced in (R1), (R3), (R5), and (R7) ultimately recombine,



where *M* is a third body which we take to be the ambient gas. The sequence of reactions leading to the exchange of isotopes between H₂O and HD may be summarized as



The magnitude of isotopic enrichment is essentially determined by (R5), the effects due to the other reactions in the sequence being much smaller. The reverse reaction,



is also important, but has not been measured. Its rate coefficient may be estimated by

$$k_6 = k_5/K_1$$

where *K*₁ is the equilibrium constant for the exchange reaction,



It is straightforward to evaluate *K*₁ using the formula and molecular constants given in Appendix A. The result is

$$K_1 = 0.72e^{717/T}.$$

Note that *K*₁ > 7, for temperatures below 300°K, and, therefore, OD is preferentially produced.

An analogous chemical scheme can be proposed for CH₄,

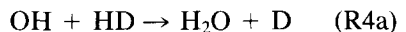
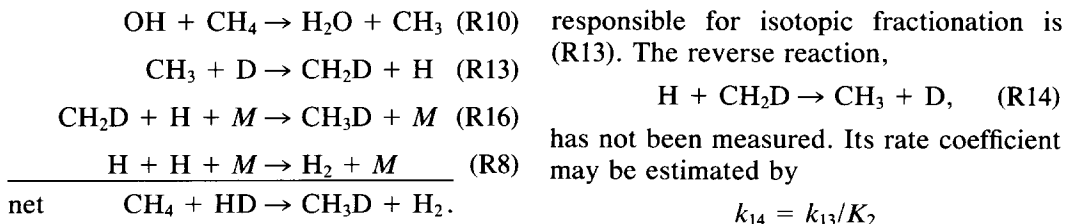


TABLE I
REACTIONS AND RATE CONSTANTS FOR THE SOLAR NEBULA

	Reaction	Rate coefficient	Reference
R1	H ₂ O + hν → H + OH	J ₁ = 1 × 10 ⁻⁹	See text
R2a	HDO + hν → H + OD	J _{2a} = $\frac{1}{2}$ J ₁	Assumed
R2b	HDO + hν → D + OH	J _{2b} = $\frac{1}{2}$ J ₁	Assumed
R3	OH + H ₂ → H ₂ O + H	k ₃ = 6.1 × 10 ⁻¹² e ^{-2030/T}	DeMore <i>et al.</i> (1985)
R4a	OH + HD → H ₂ O + D	k _{4a} = $\frac{3}{20}$ k ₃	Estimate based on Ravishankara <i>et al.</i> (1981)
R4b	OH + HD → HDO + H	k _{4b} = $\frac{3}{20}$ k ₃	Estimate based on Ravishankara <i>et al.</i> (1981)
R5	OH + D → OD + H	k ₅ = 3.3 × 10 ⁻⁹ T ^{-0.63}	Assumed based on Margitan <i>et al.</i> (1975) and Howard and Smith (1982)
R6	H + OD → OH + D	k ₆ = $\frac{k_5}{K_1}$	See text
R7	OD + H ₂ → HDO + H	k ₇ = k ₃	Assumed
R8	H + H + M → H ₂ + M	k ₈ = 1.5 × 10 ⁻²⁹ T ^{-1.3}	Tsang and Hampson (1986)
R9	H + D + M → HD + M	k ₉ = k ₈	Assumed
R10	OH + CH ₄ → H ₂ O + CH ₃	k ₁₀ = 2.4 × 10 ⁻¹² e ^{-1710/T}	DeMore <i>et al.</i> (1985)
R11	OD + CH ₄ → HDO + CH ₃	k ₁₁ = k ₁₀	Assumed
R12a	OH + CH ₃ D → H ₂ O + CH ₂ D	k _{12a} = $\frac{3}{4}$ k ₁₀	Assumed
R12b	OH + CH ₃ D → HDO + CH ₃	k _{12b} = $\frac{1}{4}$ k ₁₀	Assumed
R13	CH ₃ + D → CH ₂ D + H	k ₁₃ = 1.8 × 10 ⁻¹⁰	Brouard and Pilling (1986)
R14	H + CH ₂ D → CH ₃ + D	k ₁₄ = $\frac{k_{13}}{K_2}$	See text
R15	H + CH ₃ + M → CH ₄ + M	k ₁₅ = 2.61 × 10 ⁻²⁹	Patrick <i>et al.</i> (1980)
R16	H + CH ₂ D + M → CH ₃ D + M	k ₁₆ = k ₁₅	Assumed
R17	D + CH ₃ + M → CH ₃ D + M	k ₁₇ = k ₁₅	Assumed

Note. Rate constants for two- and three-body reactions have units cm³ sec⁻¹ and cm⁶ sec⁻¹, respectively. Photodissociation coefficients are in units of sec⁻¹, and the numerical values were computed using starlight in an optically thin region.



Note that we have also used H₂O as a catalyst for photosensitizing the dissociation of CH₄. This is not strictly necessary and other means of decomposing CH₄ would yield the same result. The crucial reaction

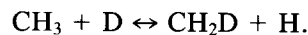
responsible for isotopic fractionation is (R13). The reverse reaction,



has not been measured. Its rate coefficient may be estimated by

$$k_{14} = k_{13}/K_2$$

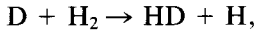
where K₂ is the equilibrium constant for



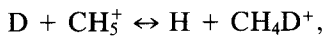
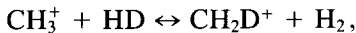
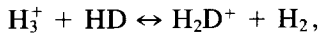
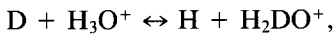
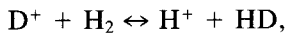
From Appendix B, we have

$$K_2 = 1.72e^{810/T}.$$

We will briefly discuss some reactions that are not included in Table I. The exchange reaction,



has been measured to 167°K by Mitchell and Le Roy (1973). Making an extrapolation to 150°K gives a rate coefficient $k = 9.5 \times 10^{-21} \text{ cm}^3 \text{ sec}^{-1}$. It can be shown that for such a small rate coefficient the reaction cannot compete with the isotope exchange reaction (R5). In this work we have not included any ion chemistry. Reactions such as



are believed to be responsible for isotopic fractionation in the interstellar medium (Dalgarno *et al.* 1973, Watson 1973a,b, Smith *et al.* 1982). The neglect of ion chemistry is due to the limited scope of this work and will be included in a more complete study in the future.

3. NEBULA MODEL

The important photochemical reactions relevant to the solar nebula are listed in Table I. There were several possible sources of ultraviolet radiation to the outer regions of the solar nebula. Emission from the protosun when its surface temperature was only 2000°K is negligible. In addition, the opacity in the midplane of the solar nebula, from micron-sized grains, would have limited the penetration of the radiation. Protosolar flares may have been an additional source (Cameron 1985) but their contribution was limited in the same way. Finally, there was a contribution from the interstellar radiation field. Mathis *et al.* (1983) have estimated ultraviolet and visible flux levels as a function of distance from the center of the galaxy. Based on their value of 3×10^8

$\text{cm}^{-2} \text{ sec}^{-1}$ for the flux of photons below 2000 Å we calculate a photolysis rate for H_2O of 10^{-9} sec^{-1} at zero optical depth. This value corresponds to a lifetime for water vapor next to the edges of the nebula of 40 years. Because of the high opacity in the midplane of the nebula, these reactions would have been confined to its outer edges. Material in the interior of the solar nebula must be brought to the surface by turbulent mixing before it can be photochemically processed. There are indications that turbulent mixing in the nebula would have mixed material in the vertical direction in about 100 years (Cameron 1985, Morfill *et al.* 1985).

Two one-box models were run using the set of reactions listed in Table I and initial conditions given in Table II. The numerical method used is described in Allen *et al.* (1981). In the first model, model A, pure hydrogen and oxygen chemistry was assumed. Only reactions (R1)–(R9) of Table I were included. The model started with a "standard" distribution of H_2 , H_2O , HD, and HDO that is supposed to simulate the solar nebula at 5 AU (Bodenheimer and Pollack 1986). Photochemistry was initiated by absorption of starlight. The model was time-marched until no further change oc-

TABLE II

PHYSICAL PARAMETERS AND INITIAL CHEMICAL COMPOSITION OF A ONE-BOX MODEL OF THE SOLAR NEBULA AT 5 AU

Temperature	150°K
Pressure	6.2×10^{-7} bar
Density	$10^{-10} \text{ g cm}^{-3}$
[H_2]	$3 \times 10^{13} \text{ cm}^{-3}$
D/H	1.7×10^{-5}
	Initial concentration (cm^{-3})
[H_2O]	1.0×10^{10}
[CH_4]	1.0×10^{10}
[HD]	1.0×10^9
[HDO]	3.4×10^5
[CH_3D]	6.8×10^5

Note. The physical model is taken from Bodenheimer and Pollack (1986).

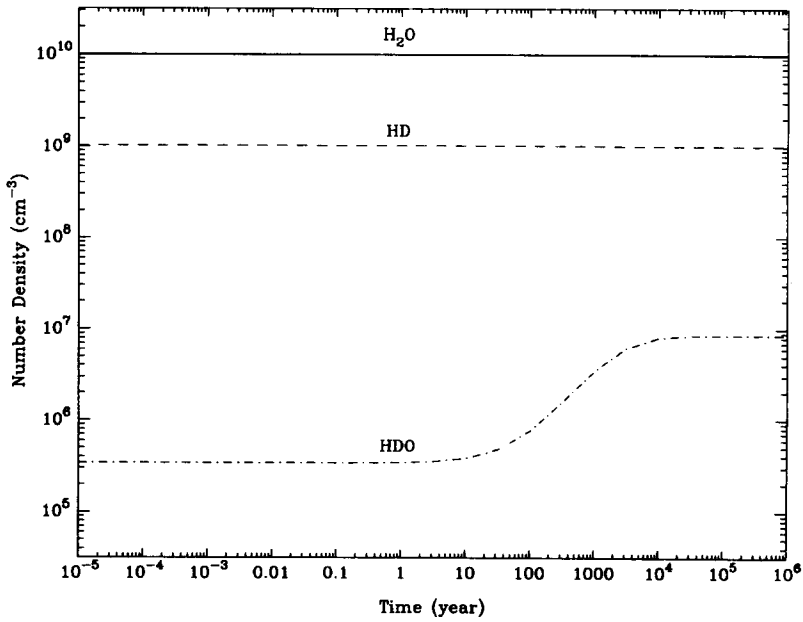


FIG. 1a. Concentrations of H₂O, HD, and HDO as a function of time in model A, which includes only reactions (R1)–(R9) in Table I.

curred. Mass for each element was rigorously conserved. The time evolution of the major species H₂O, HD, and HDO is shown

in Fig. 1a. The corresponding evolution of the radicals H, D, OH, and OD is shown in Fig. 1b. It is clear that there is a rapid build-

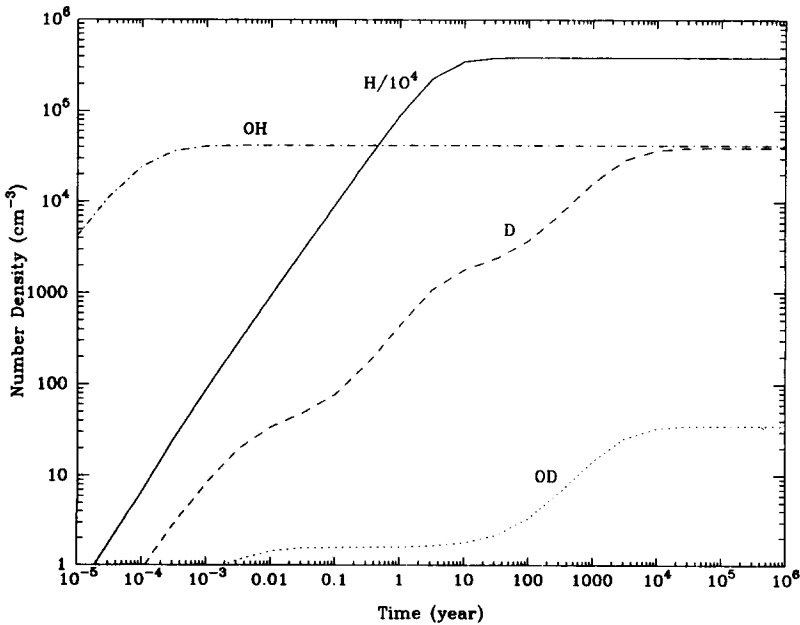


FIG. 1b. Same as Fig. 1a for the radical species H, OH, D, and OD.

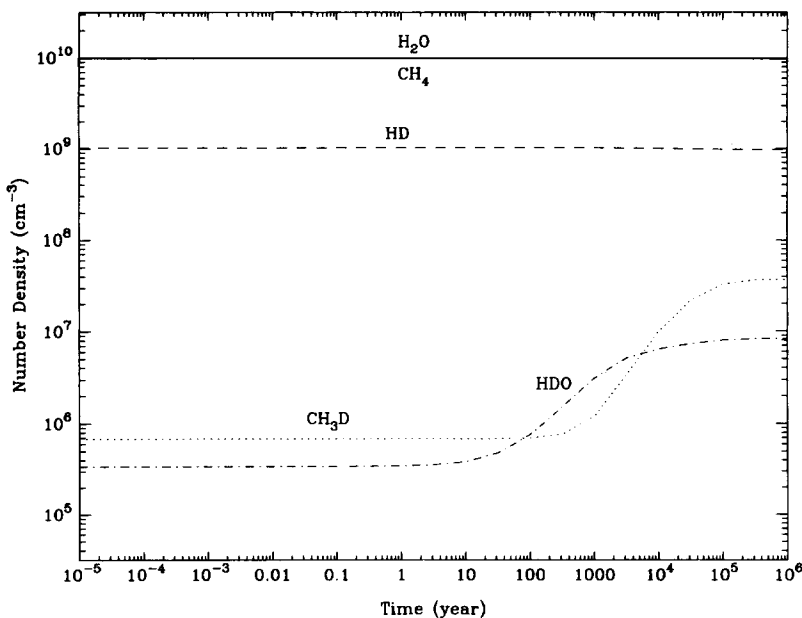


FIG. 2a. Concentrations of H_2O , CH_4 , HD , HDO , and CH_3D as a function of time in model B, which includes all the reactions in Table I.

up of HDO in less than 10^3 years. The steady-state solution is particularly simple, and can be expressed in closed form (see Appendix C). Thus, the fractionation factor r_1 is given by

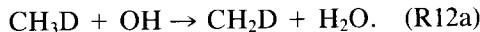
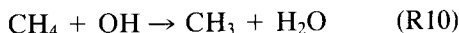
$$r_1 = \frac{[\text{HDO}]/[\text{H}_2\text{O}]}{[\text{HD}]/[\text{H}_2]} = \frac{J_1(k_{4a} + k_{4b})k_5k_7k_8}{(J_{2a} + J_{2b})k_3^2k_6k_9}$$

$$= \frac{3}{10} \frac{k_5}{k_6} = 25.7 \text{ (at } 150^\circ\text{K)}.$$

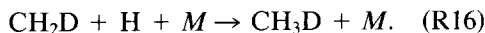
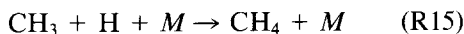
This approximation agrees with the numerical solution to within 3%.

Model B includes the photochemistry of CH_4 and CH_3D . The complete list of reactions in Table I was used in the computer simulation. The results for the major species HD , H_2O , HDO , CH_4 , and CH_3D are shown in Fig. 2a. It is clear that CH_3D built up rapidly in 10^4 years and reached steady state in about 10^5 years. The time evolution of the radical species H , D , OH , OD , CH_3 , and CH_2D is shown in Fig. 2b. The somewhat unusual behavior for CH_3 and CH_2D between 10^{-3} and 1 year requires an expla-

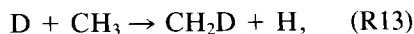
nation. The primary sources of CH_3 and CH_2D are reactions with OH ,



The loss of these radicals is primarily via reactions with H ,



Since OH has a much shorter time constant than H , it reaches steady state much earlier than H . Thus, the initial rise of CH_3 and CH_2D is caused by the large source terms (R10) and (R12a) driven by high OH concentrations. The subsequent decline in CH_3 and CH_2D is caused by the efficient sink reactions (R15) and (R16) due to the buildup of H atoms. In the case of CH_2D , there is a secondary buildup at $t > 10$ years. This arises from the exchange reaction



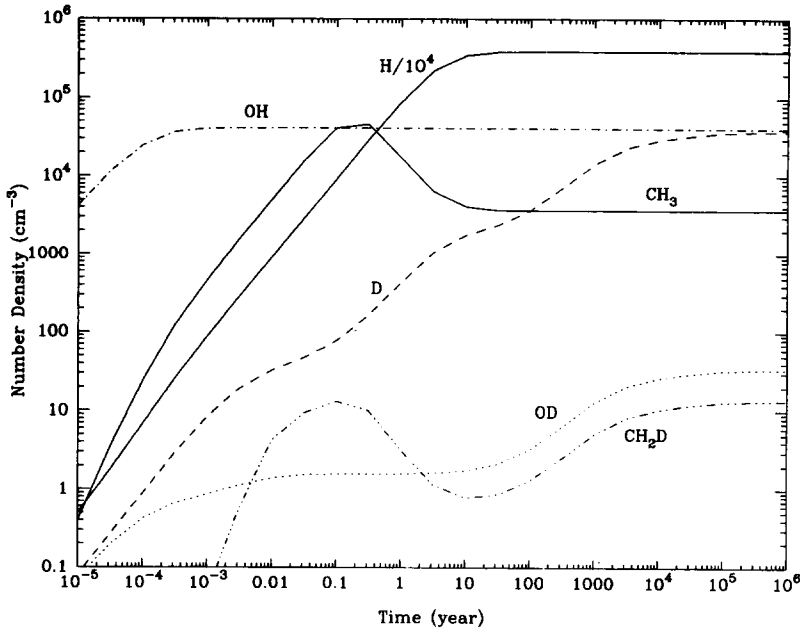


FIG. 2b. Same as Fig. 2a for the radical species H, OH, D, OD, CH₃, and CH₂D.

and the timing is essentially determined by the rate of growth of D concentrations in the model.

The fractionation factor r_2 at steady state is closely approximated by the simple expression (see Appendix C)

$$r_2 = \frac{[\text{CH}_3\text{D}]/[\text{CH}_4]}{[\text{HD}]/[\text{H}_2]} = \frac{(k_{4a} + k_{4b})k_8k_{10}k_{13}k_{16}}{k_3k_9(k_{12a} + k_{12b})k_{14}k_{15}}$$

$$= \frac{3}{10} \frac{k_{13}}{k_{14}} = 115 \text{ (at } 150^\circ\text{K)}.$$

The rate coefficients k_{15} , k_{16} , and k_{17} adopted in this study are based on the results of Patrick *et al.* (1980) and are considerably lower than the values estimated by Laufer *et al.* (1983). We have run our model using the rate coefficients of Laufer *et al.* (1983). The results for the fractionation factor and the time constant for CH₃D are not sensitive to these rate coefficients. The reason is that although a faster rate coefficient k_{15} lowers the computed abundance of CH₃ and CH₂D, this is compensated by reaction (R16), which forms CH₃D.

Using the highly accurate approximate expressions of the fractionation factors, we may estimate the values of r_1 and r_2 as a function of temperature in the nebula. The results are shown in Fig. 3. It is clear that substantial fractionation can be obtained from the kinetic fractionation mechanism for temperatures as high as 300°K.

4. CONCLUSIONS

The enrichment processes described here could have profoundly influenced the isotopic content of water in the terrestrial planets, if a large fraction of their volatiles had been added by impacts of meteorites and comets formed in the outer parts of the solar nebula (Tera *et al.* 1974, Pollack and Yung 1980). Some of the proposed chemistry described here is closely related to that of the interstellar medium (Herbst and Klemperer 1973, Allen and Robinson 1977, Prasad *et al.* 1987). We have carried out computations for the optically thin regions of the nebula. However, efficient mixing could have exposed the material in the interior of the solar nebula to starlight. We esti-

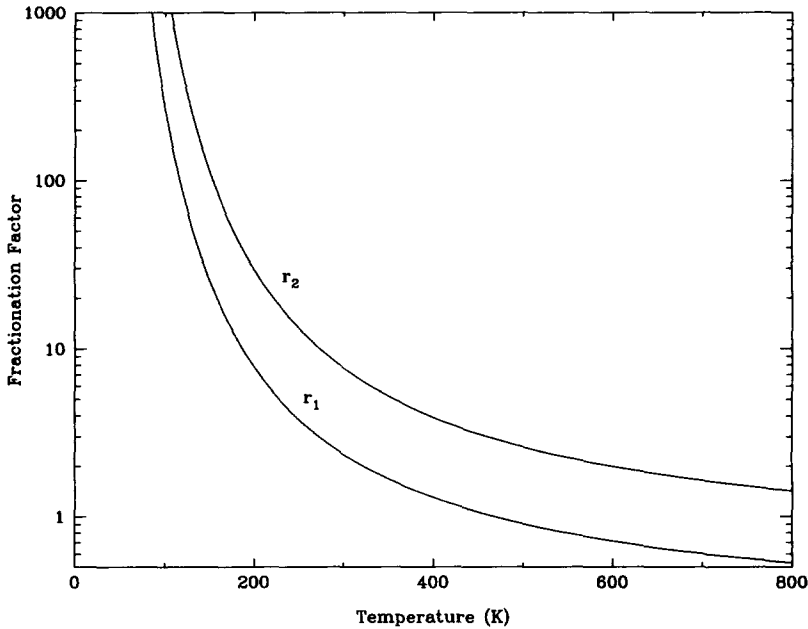


FIG. 3. Fractionation factors $r_1 = \frac{[\text{HDO}]/[\text{H}_2\text{O}]}{[\text{HD}]/[\text{H}_2]}$ and $r_2 = \frac{[\text{CH}_3\text{D}]/[\text{CH}_4]}{[\text{HD}]/[\text{H}_2]}$.

mate that the time to photochemically process the entire vertical column of material in the solar nebula at 5 AU is a few million years, while the solar nebula may have lasted for a few times 10^5 years. Photochemical reactions may not have been the major source of deuterium enrichment in outer Solar System volatiles, although they did play a role. However, if there were other sources of UV such as a nearby supernova, these reactions could have been the dominant mechanism for establishing the D to H ratio in water and methane. Thus the small bodies, such as comets, which originated in the outer Solar System, would have acquired an enhancement in D/H in H_2O of at least a factor of 10 compared to D/H in H_2 in the atmospheres of Jupiter and Saturn. Deuterium-enriched methane ice could have been a major source of volatiles in the atmospheres of Titan and the Jovian planets. Owing to the absence of a large H_2 reservoir, the deuterium enrichment in CH_4 is preserved on Titan, whereas on Jupiter and Saturn, and to a lesser extent

on Uranus and Neptune, the isotopic signature is diluted by the large H_2 reservoir.

APPENDIX A

EQUILIBRIUM CONSTANT (K_1) FOR THE REACTION $\text{D} + \text{OH} \leftrightarrow \text{OD} + \text{H}$

The equilibrium constant is given by

$$K_1 = \frac{[\text{OD}][\text{H}]}{[\text{OH}][\text{D}]}, \quad (\text{A1})$$

and can be computed using the expression

$$K_1 = \frac{Q_{\text{OD}}Q_{\text{H}}}{Q_{\text{OH}}Q_{\text{D}}} \exp\left(\frac{-E_0}{kT}\right) \\ = \left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}}\right]_{\text{vib}} \left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}}\right]_{\text{rot}} \left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}}\right]_{\text{tr}} \left[\frac{Q_{\text{H}}}{Q_{\text{D}}}\right]_{\text{tr}} \\ \exp\left(\frac{-E_0}{kT}\right), \quad (\text{A2})$$

where Q is the partition function, vib, rot, and tr denote vibrational, rotational, and translational motion, respectively, and E_0 is the difference in zero point energies between OD and OH. These formulas are

taken from standard textbooks (see for example, Davidson 1962, Benson 1976).

The vibrational energy for a diatomic molecule is given by

$$G(v) = w_e \left(v + \frac{1}{2} \right) - w_e x_e \left(v + \frac{1}{2} \right)^2 + \text{higher order terms.} \quad (\text{A3})$$

From Huber and Herzberg (1979) we have for OH, $w_e = 3737.761 \text{ cm}^{-1}$, and $w_e x_e = 84.881 \text{ cm}^{-1}$; for OD $w_e = 2720.24 \text{ cm}^{-1}$, and $w_e x_e = 44.055 \text{ cm}^{-1}$. Using (A3) we obtain $G_{\text{OH}}(0) = 1847.66 \text{ cm}^{-1}$, $G_{\text{OD}}(0) = 1349.11 \text{ cm}^{-1}$, and $E_0/kT = 717/T$.

The other quantities in (A2) can be easily evaluated

$$\left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}} \right]_{\text{vib}} \approx 1 \quad (\text{A4})$$

$$\left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}} \right]_{\text{rot}} = \left(\frac{18.91}{10.02} \right) = 1.89 \quad (\text{A5})$$

$$\left[\frac{Q_{\text{OD}}}{Q_{\text{OH}}} \right]_{\text{tr}} = \left(\frac{18}{17} \right)^{3/2} = 1.09 \quad (\text{A6})$$

$$\left[\frac{Q_{\text{H}}}{Q_{\text{D}}} \right]_{\text{tr}} = \left(\frac{1}{2} \right)^{3/2} = 0.354. \quad (\text{A7})$$

Combining all the numerical factors, we have

$$K_1 = 0.72e^{717/T}. \quad (\text{A8})$$

APPENDIX B

EQUILIBRIUM CONSTANT (K_2) FOR THE REACTION $\text{D} + \text{CH}_3 \leftrightarrow \text{CH}_2\text{D} + \text{H}$

The equilibrium constant is given by

$$K_2 = \frac{[\text{CH}_2\text{D}][\text{H}]}{[\text{CH}_3][\text{D}]} \quad (\text{B1})$$

$$= \frac{Q_{\text{CH}_2\text{D}} Q_{\text{H}}}{Q_{\text{CH}_3} Q_{\text{D}}} \exp\left(\frac{-E_0}{kT}\right)$$

$$= \left[\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right]_{\text{vib}} \left[\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right]_{\text{rot}} \left[\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right]_{\text{tr}}$$

$$\left[\frac{Q_{\text{H}}}{Q_{\text{D}}} \right]_{\text{tr}} \times N_s \exp\left(\frac{-E_0}{kT}\right), \quad (\text{B2})$$

where the symbols have the same meaning as those in Appendix A, and $N_s = 6/2 = 3$ is the symmetry number that accounts for the difference in symmetry properties between CH₃ (D_{3h}) and CH₂D (C_{2v}).

The fundamental modes of vibration for CH₃ and CH₂D and their frequencies are given in Table B-I. From the vibrational frequencies listed in this table, we have $E_0 = 6351.4 \text{ cm}^{-1} - 5788.1 \text{ cm}^{-1} = 563.3 \text{ cm}^{-1}$; $E_0/kT = 810/T$

$$\left(\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right)_{\text{vib}} \approx 1 \quad (\text{B3})$$

$$\left(\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right)_{\text{rot}} = \left[\frac{1.777 \times 2.886 \times 4.663}{3.554 \times (1.760)^2} \right]^{1/2} = 1.474 \quad (\text{B4})$$

$$\left(\frac{Q_{\text{CH}_2\text{D}}}{Q_{\text{CH}_3}} \right)_{\text{tr}} = \left(\frac{16}{15} \right)^{3/2} = 1.102 \quad (\text{B5})$$

$$\left(\frac{Q_{\text{H}}}{Q_{\text{D}}} \right)_{\text{tr}} = \left(\frac{1}{2} \right)^{3/2} = 0.354 \quad (\text{B6})$$

Combining all the numerical factors we obtain

$$k_2 = 1.72e^{810/T}. \quad (\text{B7})$$

TABLE B-I

MODES OF VIBRATION FOR CH₃ AND CH₂D, AND THEIR FREQUENCIES (WE ADOPT THE ASSIGNMENT AND NOTATION OF HERZBERG (1966))

Mode	Frequency for CH ₃ (cm ⁻¹)	Frequency for CH ₂ D (cm ⁻¹)	Reference
Symmetric stretch	$\nu_1(A_1) = 3005$	$\nu_1(A_1) = 3000$	Holt <i>et al.</i> (1984)
Umbrella	$\nu_2(A_2) = 606$	$\nu_6(B_2) = 561$	Yamada <i>et al.</i> (1981), Tan <i>et al.</i> (1972)
Asymmetric stretch	$\nu_3(E') = 3161$	$\nu_2(A_1) = 2322$	Amano <i>et al.</i> (1982)
In-plane bends	$\nu_4(E'') = 1385$	$\nu_4(B_1) = 3150$ $\nu_3(A_1) = 1380$ $\nu_5(B_1) = 1163$	Pacansky and Bargon (1975)

Note. Most of the frequencies for CH₂D are estimated with the help of Redlich-Teller product rule.

APPENDIX C
STEADY-STATE SOLUTION

By inspection of the solution at steady state ($t = \infty$), it is possible to identify the principal production and loss terms for a given species. The results are shown in Table C-I. By requiring approximate balance for the species shown in the table, we can derive analytic expressions for all the species in the model. The results are

$$[\text{OH}] = \frac{J_1 [\text{H}_2\text{O}]}{k_3 [\text{H}_2]}$$

$$[\text{H}] = \left(\frac{J_1}{k_8}\right)^{1/2} \left(\frac{[\text{H}_2\text{O}]}{M}\right)^{1/2}$$

$$[\text{D}] = \frac{(J_1 k_8)^{1/2} (k_{4a} + k_{4b}) [\text{HD}][\text{H}_2\text{O}]^{1/2}}{k_3 k_9 M^{1/2} [\text{H}_2]}$$

$$[\text{OD}] = \frac{J_1 (k_{4a} + k_{4b}) k_5 k_8 [\text{H}_2\text{O}][\text{HD}]}{k_3^2 k_6 k_9 [\text{H}_2]^2}$$

$$[\text{HDO}] = \frac{J_1 (k_{4a} + k_{4b}) k_5 k_7 k_8 [\text{H}_2\text{O}][\text{HD}]}{(J_{2a} + J_{2b}) k_3^2 k_6 k_9 [\text{H}_2]}$$

$$[\text{CH}_3] = \frac{(J_1 k_8)^{1/2} k_{10} [\text{H}_2\text{O}]^{1/2} [\text{CH}_4]}{k_3 k_{15} M^{1/2} [\text{H}_2]}$$

$$[\text{CH}_2\text{D}] = \frac{J_1^{1/2} (k_{4a} + k_{4b}) k_8^{3/2} k_{10} k_{13}}{k_3^2 k_9 k_{14} k_{15}} \frac{[\text{H}_2\text{O}]^{1/2} [\text{CH}_4][\text{HD}]}{M^{1/2} [\text{H}_2]^2}$$

$$[\text{CH}_3\text{D}] = \frac{(k_{4a} + k_{4b}) k_8 k_{10} k_{13} k_{16}}{k_3 k_9 (k_{12a} + k_{12b}) k_{14} k_{15}} \frac{[\text{CH}_4][\text{HD}]}{[\text{H}_2]}$$

TABLE C-I

PRINCIPAL PRODUCTION AND LOSS RATES FOR
SPECIES IN THE MODEL AT STEADY STATE

Species	Production rate	Loss rate
OH	$J_1[\text{H}_2\text{O}]$	$k_3[\text{OH}][\text{H}_2]$
H	$J_1[\text{H}_2\text{O}] + k_3[\text{OH}][\text{H}_2]$	$2k_8M[\text{H}]^2$
HD	$k_9M[\text{H}][\text{D}]$	$(k_{4a} + k_{4b})[\text{OH}][\text{HD}]$
OD	$k_5[\text{OH}][\text{D}]$	$k_6[\text{H}][\text{OD}]$
HDO	$k_7[\text{H}_2][\text{OD}]$	$(J_{2a} + J_{2b})[\text{HDO}]$
CH ₃	$k_{10}[\text{OH}][\text{CH}_4]$	$k_{15}M[\text{H}][\text{CH}_3]$
CH ₂ D	$k_{13}[\text{CH}_3][\text{D}]$	$k_{14}[\text{H}][\text{CH}_2\text{D}]$
CH ₃ D	$k_{16}M[\text{H}][\text{CH}_2\text{D}]$	$(k_{12a} + k_{12b})[\text{OH}][\text{CH}_3\text{D}]$

From the above expressions, we can compute the fractionation factors

$$r_1 = \frac{[\text{HDO}]/[\text{H}_2\text{O}]}{[\text{HD}]/[\text{H}_2]} = \frac{J_1(k_{4a} + k_{4b})k_5k_7k_8}{(J_{2a} + J_{2b})k_3^2k_6k_9}$$

$$= \frac{3}{10} \frac{k_5}{k_6} = 25.7 \quad (\text{at } T = 150^\circ\text{K})$$

$$r_2 = \frac{[\text{CH}_3\text{D}]/[\text{CH}_4]}{[\text{HD}]/[\text{H}_2]} = \frac{(k_{4a} + k_{4b})k_8k_{10}k_{13}k_{16}}{k_3k_9(k_{12a} + k_{12b})k_{14}k_{15}}$$

$$= \frac{3}{10} \frac{k_{13}}{k_{14}} = 115 \quad (\text{at } T = 150^\circ\text{K}).$$

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with E. M. Shoemaker, M. Allen, and J. I. Lunine. We thank R. G. Prinn for pointing out the potential importance of starlight as a means for initiating photochemistry in the Solar System. This work was partly inspired by G. J. Wasserburg's grandiose vision of geochemistry and cosmochemistry in our division although there is no conceivable correlation between this humble research and his grandiose vision. Support by NASA Grants NSG 7376 and NAGW 313 of the Planetary Atmospheres Program is gratefully acknowledged. RRF and JPP are supported by NASA NRC fellowships.

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