

ENHANCEMENT OF DEUTERATED ETHANE ON JUPITER

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ABSTRACT

We report laboratory measurements of cross sections of CH_3D and $\text{C}_2\text{H}_5\text{D}$ in the extreme ultraviolet. The results are incorporated in a photochemical model for the deuterated hydrocarbons up to C2 in the upper atmosphere of Jupiter, taking into account the fast reactions for exchanging H and D atoms between H_2 and CH_4 , $\text{H} + \text{HD} \leftrightarrow \text{D} + \text{H}_2$, $\text{CH}_3 + \text{D} \leftrightarrow \text{CH}_2\text{D} + \text{H}$. Since there is no reliable kinetics measurement for the reaction, $\text{CH}_2\text{D} + \text{H} \rightarrow \text{CH}_3 + \text{D}$, we use Yung et al.'s estimate for its rate constant. The strong temperature dependence for this reaction leads to large isotopic fractionation for CH_3D and $\text{C}_2\text{H}_5\text{D}$ in the upper atmosphere of Jupiter, where their production rates depend on the abundance of deuterated methyl radical. The model predicts that the D/H ratio in deuterated ethane is about 15 times that of the bulk atmosphere. A confirmation of this result would provide a sensitive test of the photochemistry of hydrocarbons in the atmosphere of Jupiter.

Subject heading: planets and satellites: individual (Jupiter)

1. INTRODUCTION

Extensive observations of D/H ratios of H_2 and CH_4 in the atmosphere of Jupiter have been carried out in recent years. The $(\text{D}/\text{H})_{\text{H}_2}$ ratio ranges from 2.2×10^{-5} to 2.6×10^{-5} (Encrenaz et al. 1996; Mahaffy et al. 1998). The $(\text{D}/\text{H})_{\text{CH}_4}$ ratio ranges from 1.8×10^{-5} to 2.9×10^{-5} (Feuchtgruber et al. 1999; Encrenaz et al. 1999). However, the D/H ratios for other hydrocarbons, especially C_2H_6 , are unknown. The deuterated compounds in the upper atmospheres of giant planets have not been modeled, except for HD and CH_3D (e.g., Parkinson et al. 1999). The main reasons are the lack of photochemical and kinetics data related to the deuterated compounds.

In this Letter, we present measurements of absorption cross sections of the most important deuterated hydrocarbons, CH_3D and $\text{C}_2\text{H}_5\text{D}$, in the extreme ultraviolet (EUV) and preliminary results of a photochemical model of deuterated hydrocarbons in the stratosphere of Jupiter. There are three major mechanisms for deuterium-hydrogen fractionation: (1) the difference in photolysis rates between CH_4 and CH_3D and between C_2H_6 and $\text{C}_2\text{H}_5\text{D}$; (2) the difference in molecular diffusion rates in the upper atmosphere between hydrogen and deuterium species; and (3) the different exchange rates between deuterated and nondeuterated species; e.g., the rate coefficients of the reactions $\text{H} + \text{CH}_2\text{D} \leftrightarrow \text{D} + \text{CH}_3$ are different in the forward and backward directions. Models incorporating the above mechanisms show that the $(\text{D}/\text{H})_{\text{C}_2\text{H}_6}$ may be enriched 1 order of magnitude relative to the $(\text{D}/\text{H})_{\text{CH}_4}$ in the upper atmosphere of giant planets. This result implies that $\text{C}_2\text{H}_5\text{D}$ may be readily detectable.

2. MEASUREMENTS OF CH_3D AND $\text{C}_2\text{H}_5\text{D}$ ABSORPTION CROSS SECTIONS

A double-beam absorption cell, described previously (Cheng et al. 1999), was used to determine the cross sections of CH_4 , C_2H_6 , and their deuterium isotopomers. The light source was synchrotron radiation dispersed by 1 m Seya Namioka monochromator. The monochromator was typically scanned in 0.1 nm steps

with a signal-averaging period of 2 s at each step. The absorption cell has an inner diameter of 39.5 mm and a path length of 171.7, 1133, 3288 mm (for CH_4 and CH_3D), or 553.9 mm (for C_2H_6 and $\text{C}_2\text{H}_5\text{D}$). It has a pressure port connected with five calibrated MKS Baratron capacitance pressure meters (with varied ranges 1–10,000 torr, in steps of factors of 10). To avoid interference resulting from desorbed impurities and variations in cell temperature due to irradiation, a reservoir of 600 cm³ in volume was connected to the cell.

One of the most important factors that demands great attention is to eliminate and to quantify minor impurities in samples. CH_4 , C_2H_6 (both Matheson), CH_3D , and $\text{C}_2\text{H}_5\text{D}$ (both Cambridge Isotope Laboratories, isotopic purity 98.8%) have listed chemical purities of 99.999%, 99.99%, 98.7%, and 99.8%, respectively. To purify CH_4 and CH_3D , we set up a vacuum distillation system and connected it with a White cell coupled with a Fourier transform infrared spectrometer. A copper cell ~ 15 cm³ in volume was affixed on one end to a cold head of a cryostat cooled by a compressor so that the sample may be trapped at varied temperature for distillation. From IR analysis of the purified CH_4 sample we found no evidence of H_2O or CO_2 . We estimated an upper limit of 0.2 parts per million (ppm) for these impurities. About 620 ppm of CH_3D in natural abundance was also determined. For the purified CH_3D sample, impurities CDCl_3 , H_2O , CO_2 , and other organics were successfully eliminated at the first cycle of the purification. The impurity level of CO ($\sim 0.3\%$) remained roughly the same even after repeated cycles of vacuum distillation. No spectroscopic evidence of CH_4 or higher deuterated species CH_2D_2 , CHD_3 , and CD_4 was detected. The remaining fraction of oxygen is 2970 ppm, indicating a reduction by $\sim 45\%$ after purification. It appears that traces of CO and O_2 cannot be separated from CH_4 (CH_3D) by vacuum distillation. C_2H_6 and $\text{C}_2\text{H}_5\text{D}$ were vacuum-distilled between 77 and 195 K and then slowly passed through a Pd/charcoal activated absorbant at 195 K. After purification, no CO_2 , C_2H_4 , or O_2 was detectable in the vacuum UV spectrum.

TABLE 1
PARTIAL LIST OF DEUTERIUM-RELATED HYDROCARBON REACTIONS

Base Reaction	Base Rate Coefficient	References	Branchings	Ratio
Photodissociation Reactions				
(R1) $\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H}$	J_1	1	(R2) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH}_2\text{D} + \text{H}$	3/4
(R4) $\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}_2$	J_4	2	(R3) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH}_3 + \text{D}$	1/4
(R7) $\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + 2\text{H}$	J_7	2	(R5) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CHD} + \text{H}_2$	1/2
(R10) $\text{CH}_4 + h\nu \rightarrow {}^3\text{CH}_2 + 2\text{H}$	J_{10}	2	(R6) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CH}_2 + \text{HD}$	1/2
(R13) $\text{CH}_4 + h\nu \rightarrow \text{CH} + \text{H} + \text{H}_2$	J_{13}	2	(R8) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CHD} + 2\text{H}$	1/2
(R17) $\text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H}$	J_{17}	2	(R9) $\text{CH}_3\text{D} + h\nu \rightarrow {}^1\text{CH}_2 + \text{H} + \text{D}$	1/2
(R20) $\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	J_{20}	2	(R11) $\text{CH}_3\text{D} + h\nu \rightarrow {}^3\text{CHD} + 2\text{H}$	1/2
(R23) $\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + 2\text{H}$	J_{23}	2	(R12) $\text{CH}_3\text{D} + h\nu \rightarrow {}^3\text{CH}_2 + \text{H} + \text{D}$	1/2
(R26) $\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	J_{26}	2	(R14) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CD} + \text{H} + \text{H}_2$	1/4
(R29) $\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + 2\text{H}$	J_{29}	2	(R15) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH} + \text{D} + \text{H}_2$	1/4
			(R16) $\text{CH}_3\text{D} + h\nu \rightarrow \text{CH} + \text{H} + \text{HD}$	1/2
			(R18) $\text{C}_2\text{HD} + h\nu \rightarrow \text{C}_2\text{D} + \text{H}$	1/2
			(R19) $\text{C}_2\text{HD} + h\nu \rightarrow \text{C}_2\text{H} + \text{D}$	1/2
			(R21) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{HD} + \text{H}_2$	1/2
			(R22) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{HD}$	1/2
			(R24) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{HD} + 2\text{H}$	1/2
			(R25) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{D}$	1/2
			(R27) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	2/3
			(R28) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{HD}$	1/3
			(R30) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_3\text{D} + 2\text{H}$	2/3
			(R31) $\text{C}_2\text{H}_3\text{D} + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{D}$	1/3
Chemical Reactions				
(R32) $\text{H} + {}^1\text{CH}_2 \rightarrow \text{CH} + \text{H}_2$	2.0×10^{-10}	3	(R33) $\text{H} + {}^1\text{CHD} \rightarrow \text{CD} + \text{H}_2$	1/2
(R35) $\text{H} + {}^3\text{CH}_2 \rightarrow \text{CH} + \text{H}_2$	2.66×10^{-10}	4	(R34) $\text{H} + {}^1\text{CHD} \rightarrow \text{CH} + \text{HD}$	1/2
(R38) $\text{H} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2$	$3.37 \times 10^{-20} T^3 e^{-4406/T}$	2	(R36) $\text{H} + {}^3\text{CHD} \rightarrow \text{CD} + \text{H}_2$	1/2
(R41) $\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	2.0×10^{-11}	5	(R37) $\text{H} + {}^3\text{CHD} \rightarrow \text{CH} + \text{HD}$	1/2
(R44) $\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	3.0×10^{-12}	6	(R39) $\text{H} + \text{CH}_3\text{D} \rightarrow \text{CH}_2\text{D} + \text{H}_2$	3/4
(R47) $\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	$2.35 \times 10^{-15} T^{-1.5} e^{-3725/T}$	7	(R40) $\text{H} + \text{CH}_3\text{D} \rightarrow \text{CH}_3 + \text{HD}$	1/4
(R50) $\text{CH} + \text{H}_2 \rightarrow {}^3\text{CH}_2 + \text{H}$	$3.75 \times 10^{-11} e^{-1662/T}$	8	(R42) $\text{H} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{H}_2$	2/3
(R53) $\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$5.0 \times 10^{-11} e^{200/T}$	9	(R43) $\text{H} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{HD}$	1/3
(R58) $\text{CH} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	$2.23 \times 10^{-10} e^{173/T}$	10	(R45) $\text{H} + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	3/5
(R61) ${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$	9.24×10^{-11}	11	(R46) $\text{H} + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{HD}$	2/5
(R64) ${}^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	7.0×10^{-11}	7	(R48) $\text{H} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}_2$	5/6
(R67) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	8.0×10^{-11}	3	(R49) $\text{H} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_3 + \text{HD}$	1/6
(R70) ${}^3\text{CH}_2 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	8.0×10^{-11}	3	(R51) $\text{CH} + \text{HD} \rightarrow {}^3\text{CHD} + \text{H}$	1/2
(R73) $\text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}$	$6.6 \times 10^{-20} T^{2.24} e^{-3220/T}$	12	(R52) $\text{CH} + \text{HD} \rightarrow {}^3\text{CH}_3 + \text{D}$	1/2
(R76) $\text{CH}_3 + \text{C}_2\text{H}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_2$	3.4×10^{-11}	13	(R54) $\text{CH} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
(R79) $\text{CH}_3 + \text{C}_2\text{H}_5 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4$	2.0×10^{-12}	7	(R55) $\text{CH} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
(R82) $\text{C}_2 + \text{CH}_4 \rightarrow \text{C}_2\text{H} + \text{CH}_3$	$5.05 \times 10^{-11} e^{-297/T}$	14	(R56) $\text{CD} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
(R85) $\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$	$1.2 \times 10^{-11} e^{-998/T}$	15	(R57) $\text{CD} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
(R88) $\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	$1.2 \times 10^{-11} e^{-491/T}$	16	(R59) $\text{CH} + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_3$	1/2
(R91) $\text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$	$3.5 \times 10^{-11} e^{3/T}$	15	(R60) $\text{CH} + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	1/2
(R94) $\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$5 \times 10^{-20} T^{2.63} e^{-4298/T}$	17	(R62) ${}^1\text{CH}_2 + \text{HD} \rightarrow \text{CH}_2\text{D} + \text{H}$	1/2
(R97) $2\text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	2.4×10^{-11}	13	(R63) ${}^1\text{CH}_2 + \text{HD} \rightarrow \text{CH}_3 + \text{D}$	1/2
(R100) $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	2.4×10^{-12}	7	(R65) ${}^3\text{CH}_2 + \text{CH}_2\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	4/5
			(R66) ${}^3\text{CH}_2 + \text{CH}_2\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/5
			(R68) ${}^3\text{CH}_2 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_2$	2/3
			(R69) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	1/3
			(R71) ${}^3\text{CH}_2 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_2\text{D} + \text{CH}_3$	4/5
			(R72) ${}^3\text{CH}_2 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{D}$	1/5
			(R74) $\text{CH}_3 + \text{HD} \rightarrow \text{CH}_2\text{D} + \text{H}$	1/2
			(R75) $\text{CH}_3 + \text{HD} \rightarrow \text{CH}_4 + \text{D}$	1/2
			(R77) $\text{CH}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{CH}_4 + \text{C}_2\text{HD}$	2/3
			(R78) $\text{CH}_3 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{H}_2$	1/3
			(R80) $\text{CH}_3 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{CH}_4 + \text{C}_2\text{H}_3\text{D}$	4/5
			(R81) $\text{CH}_3 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{CH}_3\text{D} + \text{C}_2\text{H}_4$	1/5
			(R83) $\text{C}_2 + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H} + \text{CH}_2\text{D}$	3/4
			(R84) $\text{C}_2 + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{D} + \text{CH}_3$	1/4
			(R86) $\text{C}_2\text{H} + \text{HD} \rightarrow \text{C}_2\text{H}_2 + \text{D}$	1/2
			(R87) $\text{C}_2\text{H} + \text{HD} \rightarrow \text{C}_2\text{HD} + \text{H}$	1/2
			(R89) $\text{C}_2\text{H} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{D}$	3/4
			(R90) $\text{C}_2\text{H} + \text{CH}_3\text{D} \rightarrow \text{C}_2\text{HD} + \text{CH}_3$	1/4
			(R92) $\text{C}_2\text{H} + \text{C}_2\text{H}_5\text{D} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4\text{D}$	5/6
			(R93) $\text{C}_2\text{H} + \text{C}_2\text{H}_5\text{D} \rightarrow \text{C}_2\text{HD} + \text{C}_2\text{H}_5$	1/6
			(R95) $\text{C}_2\text{H}_3 + \text{HD} \rightarrow \text{C}_2\text{H}_4 + \text{D}$	1/2
			(R96) $\text{C}_2\text{H}_3 + \text{HD} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{H}$	1/2
			(R98) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2\text{D} \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{HD}$	2/3
			(R99) $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3\text{D} \rightarrow \text{C}_2\text{H}_3\text{D} + \text{C}_2\text{H}_2$	1/3
			(R101) $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3\text{D}$	4/5
			(R102) $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_4\text{D} \rightarrow \text{C}_2\text{H}_5\text{D} + \text{C}_2\text{H}_4$	1/5

TABLE 1
(CONTINUED)

Base Reaction	Base Rate Coefficient	References	Branchings	Ratio
(R103) $D + H_2 \rightarrow H + HD$	$4.0 \times 10^{-18} T^{2.29} e^{-2627/T}$	18
(R104) $H + HD \rightarrow D + H_2$	$2.0 \times 10^{-18} T^{2.29} e^{-2627/T}$ (est. by $k_{103}/2$)	
(R105) $D + CH_3 \rightarrow H + CH_2D$	2.3×10^{-10}	19
(R106) $H + CH_2D \rightarrow D + CH_3$	$1.34 \times 10^{-10} e^{-810/T}$ (est. by k_{105}/K)	20

NOTE.—Rate constants are relative to nondeuterated reactions.

REFERENCES.—(1) Heck, Zare, & Chandler 1996; (2) Gladstone et al. 1996; (3) Moses et al. 2000; (4) Boullart & Peeters 1992; (5) Baulch et al. 1994; (6) Tsang & Hampson 1986; (7) Baulch et al. 1992; (8) Becker et al. 1991; (9) Berman & Lin 1983; (10) Berman et al. 1982; (11) Langford, Petek, & Moore 1983; (12) Rabinowitz et al. 1991; (13) Fahr et al. 1991; (14) Pitts et al. 1982; (15) Opansky & Leone 1996b; (16) Opansky & Leone 1996a; (17) Fahr & Laufer 1995; (18) Michael & Fisher 1990; (19) Seakins et al. 1997; (20) Yung et al. 1988.

At each wavelength, absorbance was plotted against number density and fitted to a line by least-squares to yield the absorption cross section of the sample. The resultant absorption cross sections of CH_4 and CH_3D (and C_2H_6 and C_2H_5D) in the spectral range 105–150 (and 105–161) nm are shown in Figure 1. Our CH_4 and C_2H_6 spectra are nearly identical to those of Mount, Warden, & Moos (1977). Near the threshold region, our values are smaller because our samples are free from interferences from absorption of trace impurities (M. Bahou et al. 2001, in preparation). Note that the cross sections of the heavier isotopomers deviate around 132 nm, as would be expected on the basis of the zero-point energy theory of Yung & Miller (1997).

3. KINETICS AND PHOTOCHEMICAL MODEL

On the basis of the models of Gladstone, Allen, & Yung (1996) and Lee et al. (2000), we develop a model with deuterated C1 and C2 species. We assume no difference between kinetics of deuterated hydrocarbons and their corresponding nondeuterated hydrocarbons for most reactions. However, the branching ratios for photodissociation of the deuterated species could be different. A partial list of deuterated reactions is presented in Table 1. Two pairs of fast isotope exchange reactions between HD/H_2 and CH_3D/CH_4 , $H + HD \leftrightarrow D + H_2$ and $CH_3 + D \leftrightarrow CH_2D + H$, have been included in the model. We adopt rate constants for $H + HD \leftrightarrow D + H_2$ (R103 and R104 in Table 1) suggested by Michael & Fisher (1990). Seakins et

al. (1997) determined the rate constant for reaction of methyl radical and deuterium atom, $CH_3 + D \rightarrow CH_2D + H$ (R105). Since there is no reliable kinetics measurement for its reverse reaction, $CH_2D + H \rightarrow CH_3 + D$ (R106), we use the value derived by Yung et al. (1988). These authors computed the equilibrium constant $K = 1.72e^{810/T}$ for the $D + CH_3 \leftrightarrow H + CH_2D$ exchange reaction.

4. RESULTS AND DISCUSSION

We studied several cases for testing the isotopic fractionation of hydrocarbons in the upper atmosphere of Jupiter. In all models, we assume that $[HD]/[H_2] = 4.4 \times 10^{-5}$ and the mixing ratio for CH_3D is 2.5×10^{-7} at the lower boundary. These cases include the following: (1) identical weight for H and D, no fractionation for cross sections, and exclusion of the isotopic exchange reactions; (2) different atomic weights for diffusive separation of H and D; (3) new cross sections of CH_3D and C_2H_5D ; (4) no fractionation for $D + CH_3 \leftrightarrow H + CH_2D$ exchange reactions; and (5) inclusion of fractionation for the previous exchange reactions. Results of the model calculations are shown in Figure 2. In all the figures, solid lines represent $(D/H)_{CH_4}$, and dashed lines represent $(D/H)_{C_2H_6}$. In Figure 2a

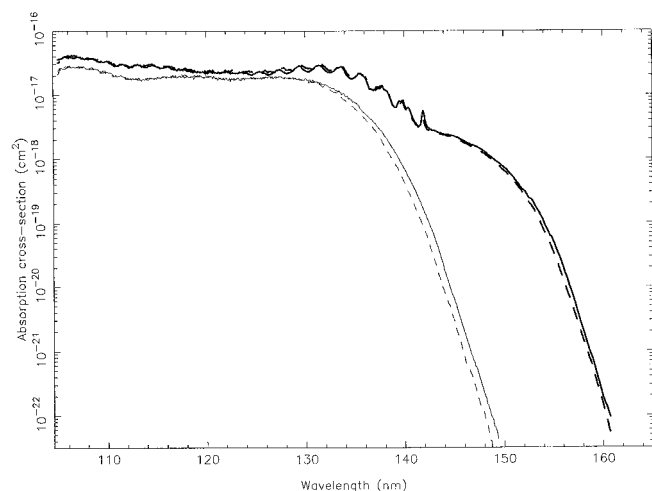


FIG. 1.—Laboratory measurements of absorption cross sections of CH_4 (thin solid line) and CH_3D (thin dashed line) for wavelengths from 105 to 150 nm and cross sections of C_2H_6 (thick solid line) and C_2H_5D (thick dashed line) for wavelengths from 105 to 161 nm. The measurements were taken at 295 K with approximately 0.1 nm resolution.

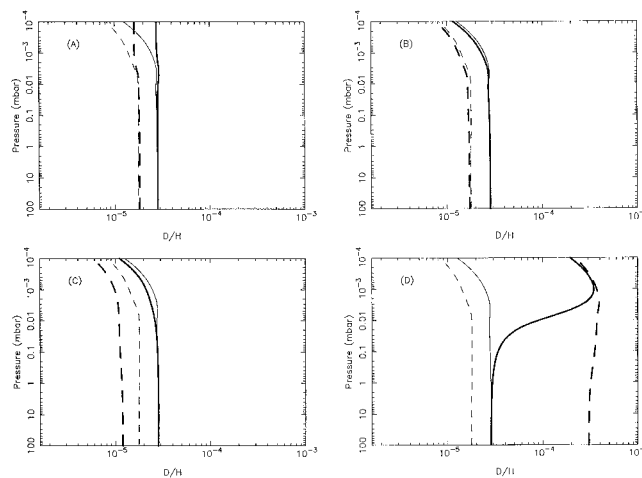


FIG. 2.—D/H ratios for CH_4 and C_2H_6 in our model. Solid lines are values of $(D/H)_{CH_4}$, and dashed lines are values of $(D/H)_{C_2H_6}$. (a) The thick lines are for the case assuming H and D species have identical masses, no difference in EUV cross sections, and no $D + CH_3 \leftrightarrow H + CH_2D$ exchange reactions. The thin lines are for the case in which H and D species have different atomic weights. (b) The thin lines denote the same case as in (a). The thick lines are for the case in which CH_3D and C_2H_5D have different cross sections. (c) The thin lines denote the same case as in (a). The thick lines are for the case with rate constants for the forward and backward reactions $D + CH_3 \leftrightarrow H + CH_2D$ in the ratio of 3 : 1. (d) The standard model. The thin lines denote the same case as in (a). The thick lines are for the case with different rate constants for both directions of the exchange reaction, as given in Table 1.

the thick lines are for the case assuming identical masses for H and D species, no difference in EUV cross sections, and no $D + CH_3 \leftrightarrow H + CH_2D$ exchange reactions. The thin lines are for the case in which H and D species have different atomic weights. Note that the decrease of D/H values in the upper atmosphere for thin lines is due to different molecular masses. In Figure 2*b*, thin lines denote the same case as in Figure 2*a*. The thick lines are for the case in which CH_3D and C_2H_5D have different cross sections, taken from Figure 1. The small difference indicates that fractionation due to photolysis is less important than that of chemical reactions (see below). The two cases described above do not include the exchange reactions $D + CH_3 \leftrightarrow H + CH_2D$.

Figure 2*c* shows the effect of including the exchange reaction $D + CH_3 \leftrightarrow H + CH_2D$ in the model. The thin lines denote the same case as in Fig. 2*a*. The thick lines are for the case in which the ratio of rate coefficients for the forward and the backward reaction is taken to be the stoichiometric value of 3 (Yung et al. 1988). A similar estimate for exchange reactions $D + H_2 \leftrightarrow H + HD$ in this case adopts the ratio of 2 : 1 rate coefficients for the forward and the backward reaction. The standard model is shown in Figure 2*d*. The thin lines denote the same case as in Figure 2*a*. The thick lines are for the case with different rate constants for both directions of the exchange

reaction, as given in Table 1. The highly enriched $(D/H)_{CH_4}$ and $(D/H)_{C_2H_6}$ values for the last case are caused by the temperature-dependent equilibrium constant for the exchange reaction. At a typical temperature of 150 K for the Jovian upper stratosphere, the equilibrium constant K for $D + CH_3 \leftrightarrow H + CH_2D$ is 381, which results in a much higher production rate for CH_2D . Consequently, the D/H ratio for C_2H_6 is an order of magnitude larger than that for CH_4 . Thus, the model predicts a result that can be tested by the determination of the abundance of C_2H_5D in the upper atmosphere of Jupiter. The nature of the temperature dependence of this fractionation factor implies even larger isotopic enrichment in the outer solar system. Thus, we expect that in the other giant planets' atmospheres, such as Saturn's, the D/H fractionation factor is even larger than in Jupiter because of their lower stratospheric temperatures. However, the fractionation may be modified by the exchange of D atoms with vibrationally excited H_2 (C. Parkinson 2000, private communication). The Cassini mission may provide observational evidence for the enrichment of deuterated ethane in the upper atmosphere of Saturn.

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REFERENCES

- Baulch, D. L., et al. 1992, *J. Phys. Chem. Ref. Data*, 21, 411
 ———. 1994, *J. Phys. Chem. Ref. Data*, 23, 847
 Becker, K. H., et al. 1991, *J. Phys. Chem.*, 95, 2390
 Berman, M. R., et al. 1982, *Chem. Phys.*, 73, 27
 Berman, M. R., & Lin, M. C. 1983, *Chem. Phys.*, 82, 435
 Boullart, W., & Peeters, J. 1992, *J. Phys. Chem.*, 96, 9810
 Cheng, B.-M., Chew, E. P., Liu, C.-P., Bahou, M., Lee, Y.-P., Yung, Y. L., & Gerstell, M. F. 1999, *Geophys. Res. Lett.*, 26, 3657
 Encrenaz, Th., et al. 1996, *A&A*, 315, L397
 Encrenaz, Th., Drossart, P., Feuchtgruber, H., Lellouch, E., Bézard, B., Fouchet, T., & Atreya, S. K. 1999, *Planet. Space Sci.*, 47, 1225
 Fahr, A., & Laufer, A. H. 1995, *J. Phys. Chem.*, 99, 262
 Fahr, A., Laufer, A., Klein, R., & Braun, W. 1991, *J. Phys. Chem.*, 95, 3218
 Feuchtgruber, H., Lellouch, E., Bézard, B., Encrenaz, Th., de Graauw, Th., & Davis, G. R. 1999, *A&A*, 341, L17
 Gladstone, G. R., Allen, M., & Yung, Y. L. 1996, *Icarus*, 119, 1
 Heck, A. J. R., Zare, R. N., & Chandler, D. W. 1996, *J. Chem. Phys.*, 104, 4019
 Langford, A. O., Petek, H., & Moore, C. B. 1983, *J. Chem. Phys.*, 78, 6650
 Lee, A. Y. T., Yung, Y. L., & Moses, J. 2000, *J. Geophys. Res.*, 105, 20,207
 Mahaffy, P. R., Donahue, T. M., Atreya, S. K., Owen, T. C., & Niemann, H. B. 1998, *Space Sci. Rev.*, 84, 251
 Michael, J. V., & Fisher, J. R. 1990, *J. Phys. Chem.*, 94, 3318
 Moses, J. I., Bézard, B., Lellouch, E., Gladstone, G. R., Feuchtgruber, H., & Allen, M. 2000, *Icarus*, 143, 244
 Mount, G. H., Warden, E. S., & Moos, H. W. 1977, *ApJ*, 214, L47
 Opansky, B. J., & Leone, S. R. 1996a, *J. Phys. Chem.*, 100, 4888
 ———. 1996b, *J. Phys. Chem.*, 100, 19904
 Parkinson, C. D., Griffioen, E., McConnell, J. C., Jaffel, L. B., Vidal-Madjar, A., Clarke, J. T., & Gladstone, G. R. 1999, *Geophys. Res. Lett.*, 26, 3177
 Pitts, W. M., et al. 1982, *Chem. Phys.*, 68, 417
 Rabinowitz, M. J., et al. 1991, *J. Phys. Chem.*, 95, 674
 Seakins, P. W., et al. 1997, *J. Phys. Chem.*, 101, 20,195
 Tsang, W., & Hampson, R. F. 1986, *J. Phys. Chem. Ref. Data*, 15, 1087
 Yung, Y. L., & Miller, C. E. 1997, *Science*, 278, 1778
 Yung, Y. L., Wen, J.-S., Friedl, R. R., Pinto, J. P., & Bayes, K. D. 1988, *Icarus*, 74, 121