Enhancement of Deuterated Ethane on Jupiter

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ABSTRACT

We report laboratory measurements of cross sections of CH₃D and C₂H₅D 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 H₂ and CH₄, H + HD ← D + H₂, CH₃ + D ← CH₂D + H. Since there is no reliable kinetics measurement for the reaction, CH₂D + H → CH₃ + 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 CH₃D and C₂H₅D 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 H₂ and CH₄ in the atmosphere of Jupiter have been carried out in recent years. The (D/H)H₂ ratio ranges from 2.2 × 10⁻⁵ to 2.6 × 10⁻³ (Encrenaz et al. 1996; Mahaffy et al. 1998). The (D/H)CH₄ 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 C₂H₆, are unknown. The deuterated compounds in the upper atmospheres of giant planets have not been modeled, except for HD and CH₃D (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, CH₃D and C₂H₅D, 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 CH₄ and CH₃D and between C₂H₆ and C₂H₅D; (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 H + CH₃D ← D + CH₄ are different in the forward and backward directions. Models incorporating the above mechanisms show that the (D/H)CH₂D may be enriched 1 order of magnitude relative to the (D/H)CH₄ in the upper atmosphere of giant planets. This result implies that C₂H₅D may be readily detectable.

2. MEASUREMENTS OF CH₃D AND C₂H₅D ABSORPTION CROSS SECTIONS

A double-beam absorption cell, described previously (Cheng et al. 1999), was used to determine the cross sections of CH₃D and C₂H₅D, 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 CH₄ and CH₃D), or 553.9 mm (for C₂H₆ and C₂H₅D). 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. CH₃D, C₂H₅D (both Matheson), CH₃D, and C₂H₅D (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 CH₃D and CH₄D, 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 CH₃D sample we found no evidence of H₂O or CO₂. We estimated an upper limit of 0.2 parts per million (ppm) for these impurities. About 620 ppm of CH₃D in natural abundance was also determined. For the purified CH₃D sample, impurities CDCl₃, H₂O, CO₂, and other organics were successfully eliminated at the first cycle of the purification. The impurity level of CO (~0.3%) remained roughly the same even after repeated cycles of vacuum distillation. No spectroscopic evidence of CH₃D or higher deuterated species CH₄D₃, CHD₄, and CD₅ was detected. The remaining fraction of oxygen is 2970 ppm, indicating a reduction by ~45% after purification. It appears that traces of CO and O₂ cannot be separated from CH₃D (CH₄D) by vacuum distillation. CH₄D and C₂H₅D were vacuum-distilled between 77 and 195 K and then slowly passed through a Pd/charcoal activated absorbant at 195 K. After purification, no CO₂, C₂H₆, or O₂ was detectable in the vacuum UV spectrum.
### TABLE 1

**Partial List of Deuterium-related Hydrocarbon Reactions**

<table>
<thead>
<tr>
<th>Base Reaction</th>
<th>Base Rate Coefficient</th>
<th>References</th>
<th>Branchings</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Photodissociation Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R1) CH₄ + hν → CH₃ + H ..</td>
<td>J₁</td>
<td></td>
<td></td>
<td>1/4</td>
</tr>
<tr>
<td>(R4) CH₄ + hν → CH₃ + H₂ ..</td>
<td>J₄</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R7) CH₄ + hν → CH₂ + 2H ..</td>
<td>J₃</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R10) CH₄ + hν → CH₃ + 2H ..</td>
<td>J₁₀</td>
<td></td>
<td></td>
<td>1/2</td>
</tr>
<tr>
<td>(R13) CH₄ + hν → CH + H + H₂ ..</td>
<td>J₁₃</td>
<td></td>
<td></td>
<td>1/4</td>
</tr>
<tr>
<td>(R17) C₂H₆ + hν → C₂H + H ..</td>
<td>J₁₇</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R20) C₂H₄ + hν → C₂H₂ + H₂ ..</td>
<td>J₂₀</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R23) C₂H₄ + hν → C₂H₂ + 2H ..</td>
<td>J₂₃</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R26) C₂H₆ + hν → C₂H₄ + H₂ ..</td>
<td>J₂₆</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td>(R29) C₂H₄ + hν → C₂H₂ + 2H ..</td>
<td>J₂₉</td>
<td></td>
<td></td>
<td>2/2</td>
</tr>
<tr>
<td><strong>Chemical Reactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R32) H + 'CH₂ → CH + H₂ ..</td>
<td>2.0 × 10⁻¹⁰</td>
<td>3</td>
<td>(R33) H + 'CHD → CD + H₂</td>
<td>1/2</td>
</tr>
<tr>
<td>(R35) H + 'CH₃ → CH + H₃ ..</td>
<td>2.66 × 10⁻¹⁰</td>
<td>4</td>
<td>(R36) H + 'CHD → CD + H₃</td>
<td>1/2</td>
</tr>
<tr>
<td>(R38) H + CH₂ → CH₃ + H₁ ..</td>
<td>3.37 × 10⁻¹⁹ T⁻¹ e⁻⁴⁹⁰⁰⁰T</td>
<td>2</td>
<td>(R39) H + CH₂D → CHD + H</td>
<td>3/4</td>
</tr>
<tr>
<td>(R41) H + CH₃ → CH₂ + H₃ ..</td>
<td>2.0 × 10⁻¹¹</td>
<td>5</td>
<td>(R42) H + CH₂D → CHD + H₂</td>
<td>1/2</td>
</tr>
<tr>
<td>(R44) H + CH₃ → CH₂ + H₂ ..</td>
<td>3.0 × 10⁻¹²</td>
<td>6</td>
<td>(R43) H + CH₃D → CH₃D + H</td>
<td>1/3</td>
</tr>
<tr>
<td>(R47) H + CH₄ → CH₂ + H₂ ..</td>
<td>2.35 × 10⁻⁹ T⁻¹ e⁻¹³⁵⁰⁰⁰T</td>
<td>7</td>
<td>(R48) H + CH₃D → CH₃D + H</td>
<td>5/6</td>
</tr>
<tr>
<td>(R50) CH + H₂ → 'CH₃ + H ..</td>
<td>3.75 × 10⁻¹¹ e⁻¹⁶⁶⁰⁰T</td>
<td>8</td>
<td>(R51) CH + HD → 'CHD + H</td>
<td>1/2</td>
</tr>
<tr>
<td>(R53) CH + CH₄ → CH₃ + H₂ ..</td>
<td>5.0 × 10⁻¹¹ e⁻⁶⁰⁰⁰⁰T</td>
<td>9</td>
<td>(R52) CH + HD → 'CHD + D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R58) CH + C₂H₆ → C₂H₅ + CH₃ ..</td>
<td>2.23 × 10⁻¹⁰ e⁻¹⁷⁰⁰T</td>
<td>10</td>
<td>(R59) CH + C₂H₂D → C₂H₃D + CH₃</td>
<td>1/2</td>
</tr>
<tr>
<td>(R61) 'CH₂ + H₂ → CH₃ + H ..</td>
<td>9.24 × 10⁻¹¹</td>
<td>11</td>
<td>(R60) CH + C₂H₂D → C₂H₃D + CHD</td>
<td>1/2</td>
</tr>
<tr>
<td>(R64) 'CH₂ + CH₃ → CH₂ + C₂H₄ + H</td>
<td>7.0 × 10⁻¹¹</td>
<td>7</td>
<td>(R62) 'CH₂ + HD → C₂H₂D + H</td>
<td>1/2</td>
</tr>
<tr>
<td>(R67) 'CH₂ + C₂H₄ → C₂H₂ + CH₃ ..</td>
<td>8.0 × 10⁻¹¹</td>
<td>3</td>
<td>(R63) 'CH₂ + HD → C₂H₂D + D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R70) 'CH₃ + CH₃ → C₂H₂ + CH₃ ..</td>
<td>8.0 × 10⁻¹¹</td>
<td>3</td>
<td>(R65) 'CH₃ + CH₃D → C₂H₃D + H</td>
<td>5/6</td>
</tr>
<tr>
<td>(R73) CH₃ + H₂ → CH₂ + C₂H₄ ..</td>
<td>6.6 × 10⁻¹⁰ T⁻¹ e⁻¹³⁵⁰⁰⁰T</td>
<td>12</td>
<td>(R66) 'CH₃ + CH₃D → C₂H₂D + D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R76) CH₆ + C₂H₄ → CH₃ + C₂H₂ ..</td>
<td>3.4 × 10⁻¹¹</td>
<td>13</td>
<td>(R77) CH₂ + C₂H₂D → CH₂ + C₂H₃D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R79) CH₆ + C₂H₄ → CH₃ + C₂H₄ ..</td>
<td>2.0 × 10⁻¹²</td>
<td>7</td>
<td>(R78) CH₂ + C₂H₂D → CH₂ + C₂H₃D</td>
<td>1/3</td>
</tr>
<tr>
<td>(R82) C₂ + CH₃ → C₂H₂ + CH₃ ..</td>
<td>5.05 × 10⁻¹¹ e⁻²⁹⁰⁰⁰T</td>
<td>14</td>
<td>(R80) CH₂ + C₂H₂D → CH₂ + C₂H₃D</td>
<td>4/5</td>
</tr>
<tr>
<td>(R85) C₃ + H₂ → C₂H₂ + H + H ..</td>
<td>1.2 × 10⁻¹¹ e⁻⁶⁰⁰⁰⁰T</td>
<td>15</td>
<td>(R81) CH₂ + C₂H₂D → CH₂ + C₂H₃D</td>
<td>1/5</td>
</tr>
<tr>
<td>(R88) C₃ + CH₄ → C₂H₂ + CH₃ ..</td>
<td>1.2 × 10⁻¹¹ e⁻⁴⁹⁰⁰⁰T</td>
<td>16</td>
<td>(R83) C₂ + CH₂D → C₂H₂D + CH₃</td>
<td>3/4</td>
</tr>
<tr>
<td>(R91) C₃ + C₂H₆ → C₂H₄ + C₂H₄ ..</td>
<td>3.5 × 10⁻¹¹ e⁻³⁷⁰⁰⁰T</td>
<td>15</td>
<td>(R84) C₂ + CH₂D → C₂H₂D + CH₂</td>
<td>1/4</td>
</tr>
<tr>
<td>(R94) C₃ + H₂ → C₃H₂ + H + H ..</td>
<td>5.0 × 10⁻²⁰ T⁻¹ e⁻²⁴⁰⁰⁰T</td>
<td>17</td>
<td>(R85) C₂H₂ + HD → C₂H₃ + D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R97) 2C₂H₆ → C₂H₄ + C₂H₄ ..</td>
<td>2.4 × 10⁻¹¹</td>
<td>13</td>
<td>(R86) C₂H₂ + HD → C₂H₃ + D</td>
<td>1/2</td>
</tr>
<tr>
<td>(R100) 2C₂H₆ → C₂H₆ + C₂H₆ ..</td>
<td>2.4 × 10⁻¹²</td>
<td>7</td>
<td>(R87) C₂H₂ + HD → C₂H₃ + D</td>
<td>1/2</td>
</tr>
</tbody>
</table>

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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 CH4 and CH3D (and C2H6 and C2H5D) in the spectral range 105–150 nm are shown in Figure 1. Our CH4 and C2H6 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., 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 et al. (1990). Seakins et al. (1997) determined the rate constant for reaction of methyl radical and deuterium atom, CH3 + D → CH3D + H (R105). Since there is no reliable kinetics measurement for its reverse reaction, CH3D + H → CH3 + D (R106), we use the value derived by Yung et al. (1988). These authors computed the equilibrium constant K = 1.72e^2.29e7 for the D + CH3 ↔ H + CH3D 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 [H]/[H2] = 4.4 × 10^-3 and the mixing ratio for CH3D is 2.5 × 10^-2 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 CH3D and C2H5D; (4) no fractionation for D + CH3 ↔ H + CH3D 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)CH3, and dashed lines represent (D/H)C2H6. In Figure 2a...

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**TABLE 1**

(CONTINUED)

<table>
<thead>
<tr>
<th>Base Reaction</th>
<th>Base Rate Coefficient</th>
<th>References</th>
<th>Branchings</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R103) D + H2 → H + HD</td>
<td>4.0 × 10^-17e^2.29e7</td>
<td>18</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(R104) H + HD → D + H2</td>
<td>2.0 × 10^-17e^2.29e7 (est. by k0/2)</td>
<td>19</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(R105) D + CH3 + H + CH3D</td>
<td>2.3 × 10^-10</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(R106) H + CH3D → D + CH3</td>
<td>1.34 × 10^-19e^2.29e7 (est. by k0/k)</td>
<td>20</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

**NOTE.**—Rate constants are relative to nondeuterated reactions.


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**FIG. 1.**—Laboratory measurements of absorption cross sections of CH4 (thin solid line) and CH3D (thin dashed line) for wavelengths from 105 to 150 nm and cross sections of CH4 (thick solid line) and CH3D (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 CH4 and C2H6 in our model. Solid lines are values of (D/H)CH4, and dashed lines are values of (D/H)C2H6. (a) The thick lines are for the case assuming H and D species have identical masses, no difference in EUV cross sections, and no fractionation of (D/H). The thin lines are for the case in which H and D species have different atomic weights. (b) The thick lines denote the same case as in (a). The thin lines are for the case in which CH3D and C2H5D have different cross sections. (c) The thin lines denote the same case as (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 
\( \text{D} + \text{CH}_3 \rightleftharpoons \text{H} + \text{CH}_2 \text{D} \) 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 2b, thin lines denote the same case as in Figure 2a. 
The thick lines are for the case in which \( \text{CH}_3 \text{D} \) and \( \text{C}_2 \text{H}_5 \text{D} \) 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 
\( \text{D} + \text{CH}_3 \rightleftharpoons \text{H} + \text{CH}_2 \text{D} \).

Figure 2c shows the effect of including the exchange reaction 
\( \text{D} + \text{CH}_3 \rightleftharpoons \text{H} + \text{CH}_2 \text{D} \) in the model. The thin lines denote 
the same case as in Fig. 2a. 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 
\((\text{Yung et al. 1988})\). A similar estimate for exchange reactions 
\( \text{D} + \text{H}_2 \rightleftharpoons \text{H} + \text{HD} \) 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 2d. The thin lines denote 
the same case as in Figure 2a. 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 \((\text{D/H})_{\text{CH}_3} \) 
and \((\text{D/H})_{\text{C}_2 \text{H}_5} \) 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 \( \text{D} + \text{CH}_3 \rightleftharpoons \text{H} + \text{CH}_2 \text{D} \) is 381, which results in a much higher production rate 
for \( \text{CH}_2 \text{D} \). Consequently, the D/H ratio for \( \text{C}_2 \text{H}_6 \) is an order of 
magnitude larger than that for \( \text{CH}_4 \). Thus, the model predicts 
a result that can be tested by the determination of the abundance 
of \( \text{C}_2 \text{H}_6 \) 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. How-
ever, the fractionation may be modified by the exchange of D 
atoms with vibrationally excited \( \text{H}_2 \) (C. Parkinson 2000, private 
communication). The Cassini mission may provide observa-
tional evidence for the enrichment of deuterated ethane in the 
upper atmosphere of Saturn.

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