Chem 245 Homework 3

Due on Tuesday, January 29

(1). Figure 4.34 gives absorption spectra of all gaseous halogens. Assuming that solar flux, \( F = 5 \times 10^{14} \text{#/cm}^2\text{/s/nm} \), is independent of wavelength in the 400 – 1000 nm window estimate the photodissociation lifetime of I\(_2\) in ambient air. Assume \( \phi = 1 \). Hint: Treat the absorption profile as a triangle in order to simplify the integration.

![Absorption Spectra](image)

**FIGURE 4.34** Absorption spectra of the halogens: (1) F\(_2\) (g), 25°C; (2) Cl\(_2\) (g), 18°C; (3) Br\(_2\) (g), 25°C; (4) I\(_2\) (g), 70–80°C; (5) I\(_2\) (g) plus 1 atm air, 70–80°C (adapted from Calvert and Pitts, 1966).

(2). Molecular constants for O\(_2\) molecule in its ground \( ^3\Sigma^+ \) electronic state have the following values: \( \nu = 1580.19 \text{ cm}^{-1} \) (harmonic frequency) and \( \nu_x = 11.98 \text{ cm}^{-1} \) (anharmonicity). Using data from table 4.5, calculate the highest possible vibrational level of O\(_2\)\( (^3\Sigma^+) \) that can be produced in photolysis of O\(_3\) at 290 nm for both channels:

\[
\begin{align*}
O_3 + h\nu &\rightarrow O_2\left(^3\Sigma^+, \nu_{\text{max}} = ?\right) + O(\text{D}) \\
O_3 + h\nu &\rightarrow O_2\left(^3\Sigma^+, \nu_{\text{max}} = ?\right) + O(\text{P})
\end{align*}
\]

<table>
<thead>
<tr>
<th>Electronic state of oxygen atom</th>
<th>( ^3\Sigma^+ )</th>
<th>( ^1\Delta )</th>
<th>( ^1\Sigma^+ )</th>
<th>( ^3\Sigma^\prime )</th>
<th>( ^3\Sigma^\prime\prime )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3\text{P} )</td>
<td>1180</td>
<td>612</td>
<td>463</td>
<td>230</td>
<td>173</td>
</tr>
<tr>
<td>( ^1\text{D} )</td>
<td>411</td>
<td>310</td>
<td>267</td>
<td>168</td>
<td>136</td>
</tr>
<tr>
<td>( ^1\text{S} )</td>
<td>237</td>
<td>199</td>
<td>181</td>
<td>129</td>
<td>109</td>
</tr>
</tbody>
</table>

*From Wayne (1987) and Okabe (1978).*
(3). Dissociation threshold for photodissociation of cold $O_2(\Sigma_g^+)\rightarrow 2O(\Sigma_g^+)$ into two $O(\Sigma_g^+)$ atoms is 242.4 nm. However, at elevated temperatures, some dissociation is easily observed at 248 nm. How many quanta of $O_2(\Sigma_g^+)$ vibrations are required to make the following process energetically possible:

$$O_2(\Sigma_g^+, v_{min} = ?) + h\nu \rightarrow O(\Sigma_g^+) + O(\Sigma_g^+)$$

(4). Atmospheric molecules conspired to stop absorbing any radiation between 1 µm and 10 µm. What important atmospheric molecules absorb in this frequency range? What effect is this molecular conspiracy going to have on the temperature of Earth's surface?

(5). Using information in Ch. 4 of FP $^2$, predict all potentially important photodissociation pathways for the following molecule:

$$OCH-CH_2-CH_2-CH_2-C(O)-OO-NO_2$$