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7.2 对于 HF 分子，HCl 分子，HBr 分子和 HI 分子的振动能级的间隔分别为3 958.4 cm^{-1}，2 885.6 cm^{-1}，2 559.3 cm^{-1}，2 230.0 cm^{-1}，计算这些分子的键力常数.

解：$\tilde{\nu} = \Delta v \tilde{\nu}_0 - \Delta v(v_1+v_2+1)\chi\tilde{\nu}_0 \approx \tilde{\nu}_0$

$\tilde{\nu}_0 = \frac{1}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

$k = \mu(2\pi c\tilde{\nu}_0)^2 = \frac{m_1 m_2}{m_1+m_2}(2\pi c\tilde{\nu}_0)^2 = \frac{A_1A_2}{A_1+A_2}\frac{(2\pi c\tilde{\nu}_0)}{N_A}$

对 HF 分子，$\tilde{\nu}_0 = 3958.4\ cm^{-1}$，得 $k = 876\ N/m$

对 HCl 分子，$\tilde{\nu}_0 = 2885.6\ cm^{-1}$，得 $k = 478\ N/m$

对 HBr 分子，$\tilde{\nu}_0 = 2559.3\ cm^{-1}$，得 $k = 382\ N/m$

对 HI 分子，$\tilde{\nu}_0 = 2230.0\ cm^{-1}$，得 $k = 291\ N/m$

7.3 $^{127}I^{35}Cl$ 的谱常数为 $\tilde{\nu}_0 = 384.18\ cm^{-1}$，$\tilde{x}_e\tilde{\nu}_0 = 1.465\ cm^{-1}$，该分子的解离能是 2.153 eV，计算：

(1) 在 $v=0$ 和 $v=1$ 之间跃迁的谱线的波数；

(2) 在 $v=1$ 和 $v=2$ 之间跃迁的谱线的波数；

(3) 分子位势曲线的深度.

解：(1) $\tilde{\nu} = \Delta v\tilde{\nu}_0 - \Delta v(v_1+v_2+1)\tilde{x}_e\tilde{\nu}_0 = \tilde{\nu}_0 - 2\tilde{x}_e\tilde{\nu}_0 = 381.25\ cm^{-1}$

(2) $\tilde{\nu} = \Delta v\tilde{\nu}_0 - \Delta v(v_1+v_2+1)\tilde{x}_e\tilde{\nu}_0 = \tilde{\nu}_0 - 4\tilde{x}_e\tilde{\nu}_0 = 378.32\ cm^{-1}$

(3) 位势深度 $E = E_{解离} + \frac{1}{2}hf = E_{解离} + \frac{1}{2}h\tilde{\nu}_0 c = 2.177\ eV$

7.9 HCl 分子有一个近红外谱带，其相邻的几条谱线的波数分别是：2 925.78 cm^{-1}，2 906.25 cm^{-1}，2 865.09 cm^{-1}，2 843.56 cm^{-1}，2 821.49 cm^{-1}，试求这个谱带的基线波数和这种分子的转动惯量.

解：$\Delta\tilde{\nu}_1 = 2925.78\ cm^{-1} - 2906.25\ cm^{-1} = 19.53\ cm^{-1}$

$\Delta\tilde{\nu}_2 = 2906.25\ cm^{-1} - 2865.09\ cm^{-1} = 41.16\ cm^{-1}$

$\Delta\tilde{\nu}_3 = 2865.09\ cm^{-1} - 2843.56\ cm^{-1} = 21.53\ cm^{-1}$

$\Delta\tilde{\nu}_4 = 2843.56\ cm^{-1} - 2821.49\ cm^{-1} = 22.07\ cm^{-1}$

$\because \Delta\tilde{\nu}_2 \approx 2\Delta\tilde{\nu}_1$，$\Delta\tilde{\nu}_1 \approx \Delta\tilde{\nu}_3 \approx \Delta\tilde{\nu}_4$

而R支 $\tilde{\nu} \approx \tilde{\nu}_0 + 2BJ_2$，$\tilde{\nu} \approx \tilde{\nu}_0 - 2BJ_1$

$\therefore \tilde{\nu}_{v_2} = \frac{1}{2}(2906.25\ cm^{-1} + 2865.09\ cm^{-1}) = 2885.67\ cm^{-1}$

$2B \approx \frac{1}{5}(2925.78\ cm^{-1} - 2821.49\ cm^{-1}) = 20.858\ cm^{-1}$

$I = \frac{h}{8\pi^2 Bc} = 2.68\times10^{-47}\ kg\cdot m^2$

7.10　Cl 原子的两同位素^{35}Cl 和^{37}Cl 分别与 H 原子化合成两种分子 H^{35}Cl 和 H^{37}Cl，试求这两种分子的振动光谱中相应光谱带基线的频率 ν_0 之比.

解：^{35}Cl：$\mu_1 = \frac{1}{N_A}\frac{A_1A_2}{A_1+A_2}$

^{37}Cl：$\mu' = \frac{1}{N_A}\frac{A_1A_2'}{A_1+A_2'}$

$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$，键力常数 k 相等时

$\frac{\nu_0'}{\nu_0} = \sqrt{\frac{\mu}{\mu'}} = \sqrt{\frac{A_1A_2}{A_1+A_2}\Big/\frac{A_1A_2'}{A_1+A_2'}} = \sqrt{\frac{37}{38}\Big/\frac{35}{36}} = 1.0007$

7.11　HBr 分子的远红外吸收光谱是一些 $\Delta\tilde{\nu} = 16.94\ \mathrm{cm}^{-1}$ 的等间隔光谱线，试求 HBr 分子的转动惯量及原子核间的距离，已知 H 和 Br 的原子量分别为 1.008 和 79.92.

解：$2B = \Delta\tilde{\omega} = 16.94\ cm^{-1}$

$I = \frac{h}{8\pi^2Bc} = 3.30\times10^{-47}\ kg\cdot m^2$

$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{m_1+m_2}{m_1m_2}I} = \sqrt{\frac{A_1+A_2}{A_1A_2}\frac{I}{N_A}} = 1.4\times10^{-10}\ m$

7.12 (1) $\lambda_{0-1} = 6 \times 1.35\ cm = 8.1\ cm$

(2) $I = \frac{h}{8\pi^2 BC}$ 而 $\Delta\tilde{\nu} = 2B$

代入可得 $I = 4.53 \times 10^{-45}\ kg \cdot m^2$

7.13 (1) $Re = \sqrt{\frac{I}{\mu}}$

$I = \frac{h}{8\pi^2 BC}$

$\Rightarrow B = 10.6\ cm^{-1}$

换算得 $B = 3.17 \times 10^5\ MHz$

(2) $E_0 = 0$

$E_1 = 2hcB = 2.624 \times 10^{-3}\ eV$

$E_2 = 6hcB = 7.8729 \times 10^{-3}\ eV$

$E_3 = 12hcB = 1.5746 \times 10^{-2}\ eV$

$E_4 = 20hcB = 2.624 \times 10^{-2}\ eV$

$E_5 = 30hcB = 3.936 \times 10^{-2}\ eV$

(3) $\frac{N_1}{N_0} = 2.71$ $\frac{N_2}{N_0} = 3.69$ $\frac{N_3}{N_0} = 3.806$

$\frac{N_4}{N_0} = 3.26$ $\frac{N_5}{N_0} = 2.4$

14 (1) $I = \frac{h}{8\pi^2 Bc}$

$r = \sqrt{\frac{I}{\mu}}$ $\Rightarrow r = 0.092\ nm$

(2) $\Delta E = 2B(J+1)$

$\Delta E_{DF} = 2B_D(J+1) = 22.1\ cm^{-1}$

$\Delta E_{TF} = 2B_T(J+1) = 15.4\ cm^{-1}$

1.15. $\nu' - \nu_1 = \nu'' + \nu_1$

$\nu' = \frac{1}{2}(\nu' - \nu'') = \frac{c}{2}\left(\frac{1}{\lambda'} - \frac{1}{\lambda''}\right) = 1.24 \times 10^{14}\ Hz$

而 $\nu_1 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ $\therefore k = (2\pi\nu_1)^2 \frac{m_H m_F}{m_H + m_F}$

$= (2\pi\nu_1)^2 \frac{A_H A_F}{N_0(A_H + A_F)} = 9.65 \times 10^2$