1. 第一次作业

我们默认使用 SI 单位制.

1.1. 1.4.

$$\frac{T}{T_0} = \exp[-n\sigma l] \in [30\%, 70\%] \implies \tag{1.1}$$

$$n = \frac{p}{kT} \wedge T = 298.15 \implies \tag{1.2}$$

$$p \in [29364.4, 99120.8]. \tag{1.3}$$

1.2. 2.1.

$$c_m[t_1] = \frac{E_0^x}{2\hbar}\langle\psi_m|d_x|\psi_n\rangle(\frac{\exp[\mathtt{i}(\omega_{mn}+\omega)t_1]-1}{\omega_{mn}+\omega} + \frac{\exp[\mathtt{i}(\omega_{mn}-\omega)t_1]-1}{\omega_{mn}-\omega}), \tag{1.4}$$

$$\frac{P_1}{P_2} \approx \frac{\dfrac{\sin^2(\frac{1}{2}(\omega_{mn}-\omega')t)}{(\omega_{mn}-\omega')^2}}{\dfrac{\sin^2(\frac{1}{2}(\omega_{mn}-\omega)t)}{(\omega_{mn}-\omega)^2}}, \tag{1.5}$$

$$\omega_{mn} = \frac{2\pi c}{\lambda} = 3.19263\mathrm{e}+15, \tag{1.6}$$

$$\frac{P_1}{P_2} = \frac{\frac{1}{4}}{735.9\mathrm{e}-28} = 3.3976\mathrm{e}+24. \tag{1.7}$$

1.3. 2.3.

$$A_{1\to 0} = \frac{64\pi^4\nu_{mn}^3}{3c^3h}|\langle 1|\vec{d}|0\rangle|^2, \tag{1.8}$$

$$\nu = 5\mathrm{e}+13, m = 1\mathrm{e}-26, \tag{1.9}$$

$$\alpha = \frac{2\pi\nu m}{\hbar}, \tag{1.10}$$

$$\langle 1|x|0\rangle = \sqrt{\frac{1}{2\alpha}} = 4.097\mathrm{e}-12, \tag{1.11}$$

$$A_{1\to 0} = \frac{64\pi^4\nu_{mn}^3}{3c^3h}(Ne)^2(\langle 1|x|0\rangle)^2 = \frac{2\pi\nu^2N^2e^2}{3c^3m\varepsilon_0} = N^2 56.339, \tag{1.12}$$

$$\tau = \frac{1}{A_{1\to 0}} = \frac{0.01775}{N^2}. \tag{1.13}$$

其中 $q = Ne$, 表示谐振子电荷量.

1.4. 2.8.

这就事电四极矩:

$$\psi_v[x] = \frac{1}{\sqrt{2^v v!}}(\frac{\alpha}{\pi})^{1/4}\exp[-\alpha\frac{x^2}{2}]H_v[\sqrt{\alpha}x], \tag{1.14}$$

Hermite 多项式具有递推关系:

$$
\begin{aligned}
zH_v[z] &= vH_{v-1}[z] + \frac{1}{2}H_{v+1}[z] \implies && (1.15)\\
z^2H_v[z] &= z(vH_{v-1}[z] + \frac{1}{2}H_{v+1}[z]) && (1.16)\\
&= vzH_{v-1}[z] + \frac{1}{2}zH_{v+1}[z] && (1.17)\\
&= v((v-1)H_{v-2}[z] + \frac{1}{2}H_v[z]) + \frac{1}{2}((v+1)H_v[z] + \frac{1}{2}H_{v+2}[z]) && (1.18)\\
&= v(v-1)H_{v-2}[z] + (v+\frac{1}{2})H_v[z] + \frac{1}{4}H_{v+2}[z], && (1.19)
\end{aligned}
$$

于是乎我们可以得到

$$
\begin{aligned}
x^2|v\rangle &= \frac{\frac{1}{\sqrt{2^v v!}}(\frac{\alpha}{\pi})^{1/4}\exp[-\alpha\frac{x^2}{2}]}{\alpha}(\sqrt{\alpha}x)^2H_v[\sqrt{\alpha}x] && (1.20)\\
&= \frac{\frac{1}{\sqrt{2^v v!}}(\frac{\alpha}{\pi})^{1/4}\exp[-\alpha\frac{x^2}{2}]}{\alpha}(v(v-1)H_{v-2}[\sqrt{\alpha}x] + (v+\frac{1}{2})H_v[\sqrt{\alpha}x] + \frac{1}{4}H_{v+2}[\sqrt{\alpha}x]) && (1.21)\\
&= \frac{v(v-1)}{\alpha\sqrt{4(v-1)v}}|v-2\rangle + \frac{1}{\alpha}(v+\frac{1}{2})|v\rangle + \frac{\sqrt{4(v+1)(v+2)}}{4\alpha}|v+2\rangle && (1.22)\\
&= \frac{1}{2\alpha}(\sqrt{v(v-1)}|v-2\rangle + (2v+1)|v\rangle + \sqrt{(v+1)(v+2)}|v+2\rangle), && (1.23)
\end{aligned}
$$

左乘 $\langle v'|$:

$$
\langle v'|x^2|v\rangle = \frac{1}{2\alpha}(\sqrt{v(v-1)}\delta_{v'(v-2)} + (2v+1)\delta_{v'v} + \sqrt{(v+1)(v+2)}\delta_{v'(v+2)}), \quad (1.24)
$$

故 $\Delta v = 0, \pm 2$ 时, 积分值不为 0.

1.5. 2.10.

$$
\begin{aligned}
|\Delta\nu_{\mathrm{D}}| &= \sqrt{\frac{8kT\ln 2}{m}}\frac{\nu_{mn}}{c} \approx 7.16233\mathrm{e}-7\sqrt{\frac{T}{M}}\nu_{mn} = 41413948\ \mathrm{s}^{-1}, && (1.25)\\
\frac{1}{\lambda} &= \frac{|\Delta\nu_{\mathrm{D}}|}{c} = 1.3814\mathrm{e}-3\ \mathrm{cm}^{-1}. && (1.26)
\end{aligned}
$$

2. 第二次作业

2.1. 3.6.

谱线间隔对应相邻能级能量差的差, 即谱线:

$$\sigma[J] = E[J+1] - E[J] = 2(J+1)hB, \tag{2.1}$$

谱线间隔:

$$\Delta\sigma = \sigma[J+1] - \sigma[J] = 2hB = \frac{hc}{\lambda} \implies \tag{2.2}$$

$$I = 3.305\mathrm{e} - 47, \tag{2.3}$$

$$\mu = \frac{M_1 M_2}{(M_1 + M_2)N_\mathrm{A}} = 1.653\mathrm{e} - 27, \tag{2.4}$$

$$d = 1.414\mathrm{e} - 10, \tag{2.5}$$

$$E[3] = 12hB = 6\frac{hc}{\lambda} = h\nu \implies \tag{2.6}$$

$$\nu = 2.687 + 12. \tag{2.7}$$

2.2. 3.8.

(a)
对于 2900 附近的波数, 对应 $v = 0 \to 1$ 及其精细结构;
对于 5668.0 和 8347.0, 对应基线 $v = 0 \to 2$ 和 $0 \to 3$.
(b)

$$\sigma_R[J] = \sigma_0[0 \to 1] + 2\widetilde{B}[1] + (3\widetilde{B}[1] - \widetilde{B}[0])J + (\widetilde{B}[1] - \widetilde{B}[0])J^2, \tag{2.8}$$

$$\sigma_P[J] = \sigma_0[0 \to 1] - (\widetilde{B}[1] + \widetilde{B}[0])J + (\widetilde{B}[1] - \widetilde{B}[0])J^2, \tag{2.9}$$

代入得

$$\sigma_R[J] = -16.5J^2 + 2008.9J + 290642.9, \tag{2.10}$$

$$\sigma_P[J] = -13.5J^2 - 2042.1J + 288622.8, \tag{2.11}$$

或者使用统一表达式:

$$\sigma[m] = \sigma_0[v \to v'] + (\widetilde{B}[v'] + \widetilde{B}[v])m + (\widetilde{B}[v'] - \widetilde{B}[v])m^2,\ m = \begin{cases} J+1, & R \\ -J, & P \end{cases} \tag{2.12}$$

$$\sigma[m] = -14.75035511J^2 + 2035.786151J + 288618.5234, \tag{2.13}$$

$$\widetilde{B}[1] = 1010.52 = \widetilde{B}_\mathrm{e} - \frac{3}{2}\widetilde{\alpha}_\mathrm{e}, \tag{2.14}$$

$$\widetilde{B}[0] = 1025.27 = \widetilde{B}_\mathrm{e} - \frac{1}{2}\widetilde{\alpha}_\mathrm{e}, \tag{2.15}$$

$$\widetilde{B}_\mathrm{e} = \frac{3\widetilde{B}[0] - \widetilde{B}[1]}{2} = 1032.645 = \frac{h}{8\pi^2 \mu r_0^2 c}, \tag{2.16}$$

$$\mu = 1.6144\mathrm{e}-27 \implies \tag{2.17}$$

$$r_0 = \sqrt{\frac{h}{8\pi^2 \mu c \widetilde{B}_\mathrm{e}}} = 1.296\mathrm{e}-10. \tag{2.18}$$

(c)
此时需考虑振动基线:

$$\sigma[0 \to v'] = \widetilde{\nu}_\mathrm{e} v' - \widetilde{\nu}_\mathrm{e}\chi_\mathrm{e} v'(v'+1), \tag{2.19}$$

根据 (b) 可算得 $\sigma_0[v = 0 \to 1] = 288618.5$, 差分

$$\Delta\sigma_0[0] = 288618.5, \tag{2.20}$$

$$\Delta\sigma_0[1] = 278181.5, \tag{2.21}$$

$$\Delta\sigma_0[2] = 267900, \tag{2.22}$$

$$\Delta\sigma_0[v] = \widetilde{\nu}_\mathrm{e} - 2(v+1)\widetilde{\nu}_\mathrm{e}\chi_\mathrm{e}, \tag{2.23}$$

$$\Delta\sigma_0[v] = -10359.25v + 288592.6, \tag{2.24}$$

$$\widetilde{\nu}_\mathrm{e}\chi_\mathrm{e} = 5179.625, \tag{2.25}$$

$$\widetilde{\nu}_\mathrm{e} = 293772.2, \tag{2.26}$$

$$\nu_\mathrm{e} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \implies \tag{2.27}$$

$$k = \mu(2\pi\nu_\mathrm{e})^2 = 494.35. \tag{2.28}$$

(d)

$$D_0 = hc\left(\frac{\widetilde{\nu}_\mathrm{e}^2}{4\widetilde{\nu}_\mathrm{e}\chi_\mathrm{e}} - \frac{\widetilde{\nu}_\mathrm{e}}{2}\right) = 7.9827\mathrm{e}-19, \tag{2.29}$$

$$E_\mathrm{v}[0] = hc\left(\frac{\widetilde{\nu}_\mathrm{e}}{2} - \frac{\widetilde{\nu}_\mathrm{e}\chi_\mathrm{e}}{4}\right) = 2.9816\mathrm{e}-20, \tag{2.30}$$

$$D_\mathrm{e} = D_0 + E_\mathrm{v}[0] = 8.2719\mathrm{e}-19. \tag{2.31}$$

(e) 不知道.

2.3. 3.12.

(1)

$$\begin{array}{ccccccccc} J & 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ \Delta\sigma_R[J] & 3774 & 3741 & 3702 & 3670 & 3631 & 3598 & 3559 & 3528 \end{array} \tag{2.32}$$

$$\widetilde{B}[1] = \widetilde{B}_\mathrm{e} - \frac{3}{2}\widetilde{\alpha}_\mathrm{e}, \tag{2.33}$$

$$\widetilde{B}[0] = \widetilde{B}_{\mathrm{e}} - \frac{1}{2}\widetilde{\alpha}_{\mathrm{e}}, \tag{2.34}$$

$$\Delta\sigma_R[J] = -35.512J + 3774.667, \tag{2.35}$$

$$\Delta\sigma_R[J] = (3\widetilde{B}[1] - \widetilde{B}[0]) + (B[1] - B[0])(2J+1) = 2(B[1] - B[0])J + 4B[1] - 2B[0], \tag{2.36}$$

$$\widetilde{\alpha}_{\mathrm{e}} = \widetilde{B}[0] - \widetilde{B}[1] = -\frac{-35.512}{2} = 17.756, \tag{2.37}$$

$$\begin{cases} 2(B[1] - B[0]) = -35.512, \\ 4B[1] - 2B[0] = 3774.667, \end{cases} \tag{2.38}$$

$$B[1] = 1905.0895, B[0] = 1922.8455, \tag{2.39}$$

$$\widetilde{B}_{\mathrm{e}} = \frac{3B[0] - B[1]}{2} = 1931.7235. \tag{2.40}$$

(2)

$$J_{\mathrm{h}} = \frac{2B[1] - B[0]}{B[0] - B[1]} = 106. \tag{2.41}$$

2.4. 3.16.

这在 3.12. 中已经处理过了, 其中 2906.25 为 $R[0]$, 2865.14 为 $P[1]$. 转动常数这 subscript 看不清.

2.5. 3.17.

$$\psi_{\mathrm{ns}} = \begin{cases} |1[a]\rangle|1[b]\rangle, \\ |0[a]\rangle|0[b]\rangle, \\ |-1[a]\rangle|-1[b]\rangle, \\ \frac{1}{\sqrt{2}}(|1[a]\rangle|0[b]\rangle + |0[a]\rangle|1[b]\rangle), \\ \frac{1}{\sqrt{2}}(|1[a]\rangle|-1[b]\rangle + |-1[a]\rangle|1[b]\rangle), \\ \frac{1}{\sqrt{2}}(|-1[a]\rangle|0[b]\rangle + |0[a]\rangle|-1[b]\rangle), \\ \frac{1}{\sqrt{2}}(|1[a]\rangle|0[b]\rangle - |0[a]\rangle|1[b]\rangle), \\ \frac{1}{\sqrt{2}}(|1[a]\rangle|-1[b]\rangle - |-1[a]\rangle|1[b]\rangle), \\ \frac{1}{\sqrt{2}}(|-1[a]\rangle|0[b]\rangle - |0[a]\rangle|-1[b]\rangle), \end{cases} \tag{2.42}$$

前六个对称.

2.6. 3.18.

$$
\begin{array}{cccc}
J & \mathrm{H}_2(I=\frac{1}{2}) & \mathrm{D}_2(I=1) & \mathrm{C}_2(I=0) \\
0 & 1 & 6 & 1 \\
1 & 9 & 9 & 0 \\
2 & 5 & 30 & 5
\end{array}
\tag{2.43}
$$

3. 第三次作业

3.1. 4.2.

氢化物, 使用联合原子:

$$\mathrm{NaH}: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2;\ {}^1\Sigma^+ \tag{3.1}$$
$$\mathrm{NaH}^*: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^1(3p\sigma)^1;\ {}^1\Sigma^+,\ {}^3\Sigma^+ \tag{3.2}$$
$$\mathrm{BeH}: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^1;\ {}^2\Sigma^+ \tag{3.3}$$
$$\mathrm{BeH}^*: (1s\sigma)^2(2s\sigma)^1(2p\sigma)^2;\ {}^2\Sigma^+ \tag{3.4}$$
$$\mathrm{BeH}^*: (1s\sigma)^2(2s\sigma)^2(2p\pi)^1;\ {}^2\Pi \tag{3.5}$$
$$\mathrm{OH}: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3;\ {}^2\Pi \tag{3.6}$$
$$\mathrm{OH}^*: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^1(2p\pi)^4;\ {}^2\Sigma^+ \tag{3.7}$$
$$\mathrm{HCl}: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2(3p\sigma)^2(3p\pi)^4;\ {}^1\Sigma^+ \tag{3.8}$$
$$\mathrm{HCl}^*: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2(3p\sigma)^2(3p\pi)^3(3d\sigma)^1;\ {}^1\Pi,\ {}^3\Pi \tag{3.9}$$
$$\mathrm{AlH}: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2(3p\sigma)^2;\ {}^1\Sigma^+ \tag{3.10}$$
$$\mathrm{AlH}^*: (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^4(3s\sigma)^2(3p\sigma)^1(3p\pi)^1;\ {}^1\Pi,\ {}^3\Pi. \tag{3.11}$$

3.2. 4.3.

分离原子:

$$\mathrm{N_2}: (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4, \tag{3.12}$$

(1)

$$\mathrm{N_2^*}: (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^1(\pi_u 2p)^4(\pi_g 2p)^1;\ {}^1\Pi_g,\ {}^3\Pi_g. \tag{3.13}$$

(2)

$$\mathrm{N_2^*}: (\sigma_g 1s)^2(\sigma_u 1s)^2(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^1;\ {}^1\Sigma_u^+,\ {}^3\Sigma^+,\ {}^1\Sigma^-,\ {}^3\Sigma^-,\ {}^1\Delta,\ {}^3\Delta. \tag{3.14}$$

3.3. 4.5.

(1)

$$\pi^3\delta: \tag{3.15}$$
$$m_{l1} = \pm 1, m_{l2} = \pm 2, \tag{3.16}$$
$$s_1 = \frac{1}{2}, s_2 = \frac{1}{2}, \tag{3.17}$$
$$\Lambda = 1, 3, \tag{3.18}$$
$$S = 0, 1, \tag{3.19}$$
$$^1\Pi,\ ^3\Pi,\ ^1\Phi,\ ^3\Phi. \tag{3.20}$$

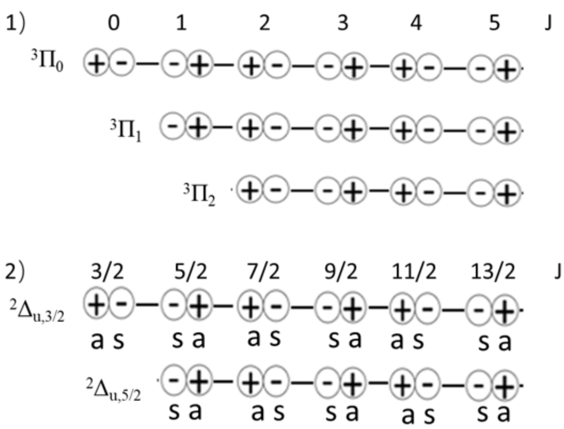
(2)

$$\pi^2\sigma\sigma: \tag{3.21}$$
$$(^3\Sigma^-,\ ^1\Sigma^+,\ ^1\Delta) \xrightarrow{\sigma} (^4\Sigma^-,\ ^2\Sigma^-,\ ^2\Sigma^+,\ ^2\Delta) \xrightarrow{\sigma} (^5\Sigma^-,\ ^3\Sigma^-,\ ^3\Sigma^-,\ ^1\Sigma^-,\ ^3\Sigma^+,\ ^1\Sigma^+,\ ^1\Delta,\ ^3\Delta). \tag{3.22}$$

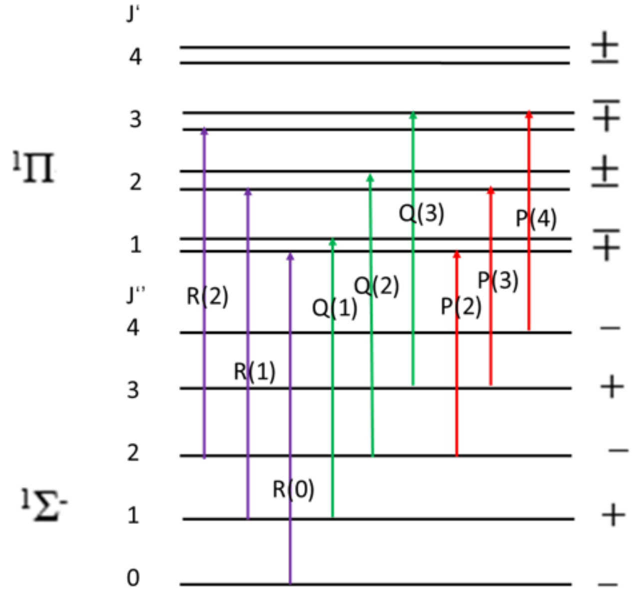
3.4. 4.8.

Case (a):
此时 $\Sigma = \pm\frac{1}{2} \implies \Omega = \frac{3}{2}, \frac{5}{2}$,
于是分裂为两组, J 分别从 $\frac{3}{2}, \frac{5}{2}$ 一次递增 1.
Case (b):
此时 $J = N \pm \frac{1}{2}$, $N = 2, 3, 4, \cdots$, 故每一个都分裂为两个子能级.

4.9 画出 1）$^3\Pi$，2）$^2\Delta_u$ 态在（a）种耦合情况下的对称性纲要图（考虑 Λ 双重性）



4.10 画出 $^1\Pi \leftarrow {}^1\Sigma^-$ 转动能级跃迁图（考虑 $^1\Pi$ 态的 Λ 分裂），标出 P（J）、Q（J）、R（J）。



4.11 画出 $^1\Sigma^-_g \leftarrow {}^1\Pi_u$ 的转动能级跃迁的纲要图，标明 P、Q、R 支，并指出其中哪些谱线消失，如果是玻色子（I=1），用虚线表示弱强度谱线。