Microscopic rate coefficients:

$$k(E) = \frac{Q^*_{rot}}{Q_{rot}} \frac{W^*(E^*)}{h\rho(E)} \tag{4.1.5}$$

$$W(E) \sim W_{cl}(E_{cl}) = \int_0^{E_{cl}} c^{(n_v)}_{vib-cl} \varepsilon_{cl}^{n_v - 1} d\varepsilon_{cl} = c^{(n_v)}_{sum-cl} E_{cl}{}^{n_v} \tag{4.1.10}$$

⟨Whitten–Rabinovich approximation⟩

$$W(E) \sim c^{(n_v)}_{sum-cl} [E + (1 - \beta\omega) E_{ZP}]^{n_v} \tag{4.1.11}$$

$$\beta = \frac{n_v - 1}{n_v} \frac{\langle \nu^2 \rangle}{\langle \nu \rangle^2}, \quad \begin{cases} \omega^{-1} = 5\varepsilon' + 2.73(\varepsilon')^{0.5} + 3.5100 & for \quad \varepsilon' = 0.1 - 1.0 \\ \log_{10} \omega = -1.0506(\varepsilon')^{0.25} & for \quad \varepsilon' = 1.0 - 8.0 \end{cases}, \quad \varepsilon' = E / E_{ZP}$$

$$\rho(E) = \frac{dW}{dE} \sim c^{(n_v)}_{viv-cl} [E + (1 - \beta\omega) E_{ZP}]^{n_v - 1} \left(1 - \beta \frac{d\omega}{d\varepsilon'}\right) \tag{4.1.12}$$

Source list 1. A FORTRAN subroutine for the 'direct count'

```
C-----------------------------------------------------------------------
      SUBROUTINE DCOUNT(NUMV,JFRQ,NUMG,DENS,SUMS)
C       Direct count (Beyer-Swinehart algorithm)
C NUMV   : number of vibrators
C JFRQ() : vibrational frequencies (energy grain unit; integer)
C NUMG   : number of energy grains
C DENS() : density of states (subscript 1 corresponds to E=0)
C SUMS() : sum of states
C-----------------------------------------------------------------------
      PARAMETER (MAXVIV=50,MAXGRN=80000)
      INTEGER NUMV,NUMG,JFRQ(MAXVIV),IV,IG,JFR,NSTT,JG
      DOUBLE PRECISION DENS(MAXGRN),SUMS(MAXGRN)
C     ----- Reset matrices
      DO IG=1,NUMG
        DENS(IG)=0.0D0
        SUMS(IG)=1.0D0
      ENDDO
      DENS(1)=1.0D0
C     ----- Beyer-Swinehart direct count
      DO IV=1,NUMV
        JFR=JFRQ(IV)
        NSTT=JFR+1
        DO IG=NSTT,NUMG
          JG=IG-JFR
          DENS(IG)=DENS(IG)+DENS(JG)
          SUMS(IG)=SUMS(IG)+SUMS(JG)
        ENDDO
      ENDDO
      RETURN
      END
```

Problem-4.2 ——————————————

1) Evaluate $k(E)$ (eq. 4.1.5) for $CH_3CH_2I \rightarrow CH_2{=}CH_2 + HI$ at E = 19000 and 25000 cm^{-1}.
   Compare the results of classical approximation [(2.3.5), (4.1.10)] and Whitten–Rabinovitch approximation [(4.1.11), (4.1.12)].

   ⟨CH_3CH_2I⟩ vib. freq.: 3000(5), 1430(3), 1280(3), 1050(2), 940, 760, 500, 240, 200 cm^{-1}
   rot. const.: 0.0943, 0.101, 0.956 cm^{-1}

   ⟨TS⟩ vib. freq.: 3000(4), 1770, 1450, 1370(3), 1120, 1090, 1050, 930, 570, 330, 250, 170 cm^{-1}
   rot. const.: 0.0609, 0.0644, 0.774 cm^{-1}

   Dissociation threshold energy E_0 = 17800 cm^{-1}

2) [OPTION] Evaluate the density/sum of states by *direct count*, and compare with above results.

Unimolecular Reactions

Lindemann: $k = \dfrac{k_0 k_\infty [\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty}$ (4.2.4)

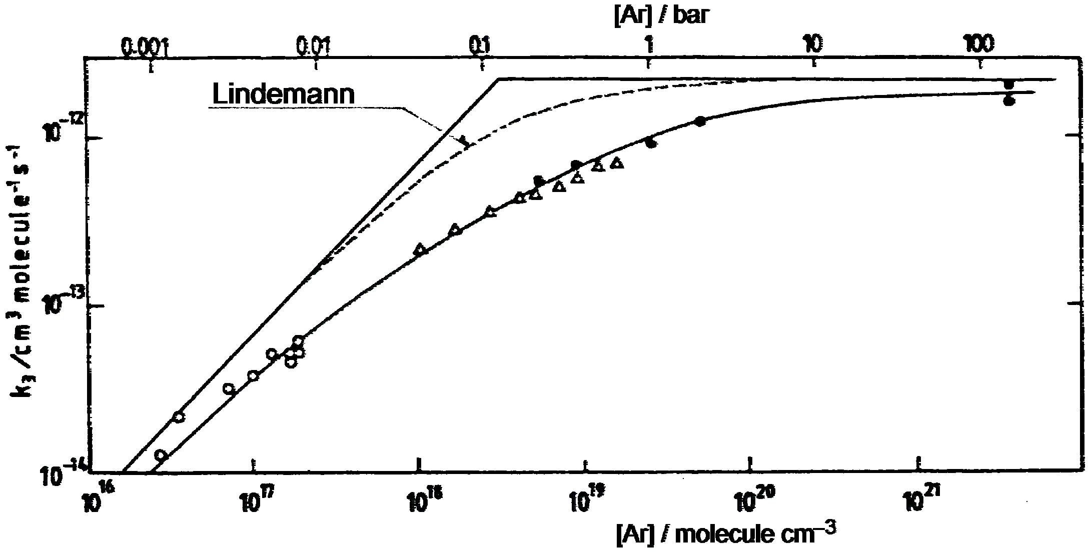

Fig. 4.4 Rate constant for CH_3 + O_2 recombination reaction

Troe's formula: $k = \dfrac{k_0 k_\infty [\mathrm{M}]}{k_0[\mathrm{M}] + k_\infty} F$ (4.2.6)

RRKM theory

RRKM: $k = \displaystyle\int_{E_0}^{\infty} k(E) g(E) dE = \frac{1}{Q_\mathrm{A}} \int_{E_0}^{\infty} k(E) \frac{\rho(E)\exp(-E/k_\mathrm{B}T)}{1 + k(E)/k_d[\mathrm{M}]} dE$ (4.3.3)

H.P.L.: $k_\infty = \displaystyle\int_{E_0}^{\infty} k(E) F(E) dE = \frac{k_\mathrm{B}T}{h} \frac{Q^*_{rot} Q^*}{Q_{rot} Q} \exp\left(-\frac{E_0}{k_\mathrm{B}T}\right)$ = TST (4.3.5)

L.P.L.: $k_0 = k_d \displaystyle\int_{E_0}^{\infty} F(E) dE = \int_{E_0}^{\infty} k_a(E) dE$ (4.3.6)

Strong coll. RRKM: $k_d = k_d^{\mathrm{SC}} = \Omega^{(2,2)*}_{\mathrm{A-M}} \pi \sigma^2_{\mathrm{A-M}} \sqrt{\dfrac{8k_\mathrm{B}T}{\pi\mu_{\mathrm{A-B}}}}$ (4.3.8)

$$\Omega^{(2,2)*}_{\mathrm{A-M}} \sim \left[0.70 + 0.52\log_{10}\left(k_\mathrm{B}T/\varepsilon_{\mathrm{A-M}}\right)\right]^{-1}, \quad \sigma_{\mathrm{A-M}} \sim (\sigma_\mathrm{A} + \sigma_\mathrm{M})/2, \quad \varepsilon_{\mathrm{A-M}} \sim \sqrt{\varepsilon_\mathrm{A}\varepsilon_\mathrm{B}}$$

Weak coll. RRKM: $k_d = k_d^{\mathrm{WC}} = \beta_c\, k_d^{\mathrm{SC}}$ (4.3.9)

Problem-4.4 [OPTION] ————————

1) By using the weak collision corrected RRKM theory, calculate k_0, k_∞, and k at [M] = $[\mathrm{M}]_c$ at 800 K for the reaction in the problem-4.2. Calculate ρ and W by the Whitten-Rabinovich approximation or by the direct count. Assume β_c = 0.2 and M = Ar, and use $\sigma(CH_3CH_2I)$ = 5.3 Å, σ(Ar) = 3.5 Å, $\varepsilon(CH_3CH_2I)$ / k_B = 320 K, and ε(Ar) / k_B = 93 K.
2) Plot the weak collision vibrational energy distribution, $g^{\mathrm{WC}}(E)$, at [M] = $[\mathrm{M}]_c$ against E, and compare it with the Boltzmann distribution, $F(E)$.