\[ \text{O}_3 (\tilde{X}^1A^\prime) + \hbar \omega \rightarrow \text{O}_3^* \rightarrow \text{O} + \text{O}_2 (v, j) \]

**Absorption Bands**

**Electronic Product Channels**

- \( \lambda < 310 \text{ nm} \rightarrow \text{O}^{(1)}D + \text{O}_2 (a^1\Delta_g) \)
- \( \lambda < 411 \text{ nm} \rightarrow \text{O}^{(1)}D + \text{O}_2 (X^3\Sigma_g^-) \)
- \( \lambda < 463 \text{ nm} \rightarrow \text{O}^{(3)}P + \text{O}_2 (b^1\Sigma^+_g) \)
- \( \lambda < 612 \text{ nm} \rightarrow \text{O}^{(3)}P + \text{O}_2 (a^1\Delta_g) \)
- \( \lambda < 1180 \text{ nm} \rightarrow \text{O}^{(3)}P + \text{O}_2 (X^3\Sigma_g^-) \)

*black: spin-allowed*

*red: spin-forbidden*

From Reinhard Schinke
From Reinhard Schinke
Autocorrelation fct.: \( S(t) = \langle \Phi_B(0) | \Phi_B(t) \rangle \)

- overlap between initial \((t = 0)\) and moving wave packet
- reflects the \textit{dynamics} of wave packet as it moves on the PES

- \textit{recurrences} A,B,\ldots due to trapped motion above the two \(C_s\) potential wells
- related to \textit{periodic orbits}
- \textit{periods} agree well with experimental ones (obtained from measured absorption spectrum), \textit{amplitudes} do not!

From Reinhard Schinke
Absorption spectrum

\[ \sigma(E) \propto \int dt \ S(t) \ e^{-iEt} \]

(time – energy Fourier Transformation)

- Structures (resonances) in (a) are due to recurrences; much stronger than in measured spectrum.

- Non-adiabatic coupling and thermal broadening \((J \neq 0)\) will damp them!

- Averaged spectrum \((t < 25 \text{ fs})\) agrees well with measured spectrum, including absolute value
– one-to-one correspondence between measured and calculated spectrum
– agreement gradually worsens at higher energies (failure of PES)
Lasers: $N_2 \gg N_1$

2

$B_{23} W_p(\omega)$

$A_{21}$

$A_{23}$

$B_{21} W(\omega)$

1

$A_{13}$

3
Lasers: $N_2 \gg N_1$

\[ B_{23} W_p(\omega) \]

\[ A_{21} \text{ slow} \]

\[ A_{23} \]

\[ B_{21} W(\omega) \]

**Pump**

**Lase**
Mixture of helium and neon gas

100% reflective
High voltage for pumping
99% reflective
Helium is "pumped" up to excited states by electrical discharge.

Energy transfer by collision elevates neon atoms into a metastable state.

Laser transition

Spontaneous emissions deplete the lower level to help maintain the population inversion.

Helium

Neon

20.61 eV

20.66 eV

18.70 eV

632.8 nm
Nd$^{3+}$:Y$_3$Al$_5$O$_{12}$ (YAG)
Cavity—2 mirrors separated by $n\lambda/2$

Lasers characterized by:
- Directionality
- Monochromatic
- Brightness
- Coherence

Discuss: Threshold
Linewidths
Homogeneous Broadening:
Affects every molecule the same way

e.g. time energy uncertainty principle and pressure broadening

\[ \delta E \delta \tau \geq h \quad \delta \nu \delta \tau \geq 1 \]

sets a minimum linewidth of \( \delta \omega \geq \tau^{-1} \)

Expressed as \( e^{-t/\tau} \) decay of final state probability the corresponds after Fourier transform to a Lorentzian lineshape

\[ I_L(\omega) = \frac{I_{\text{max}}/4\tau^2}{(\omega - \omega_0)^2 + (1/4\tau)^2} \]

FWHM=\( \tau \)
Linewidths

Inhomogeneous broadening:

Collection of molecules have a distribution of transition energies. Typically given by statistics of different molecular environments and described by Gaussian functions.

\[ I_G(\omega) = I_{\text{max}} e^{-(\omega-\omega_0)^2/2\sigma^2} \]

FWHM=\(2\sigma\sqrt{(2\ln2)}\)

e.g. Doppler Broadening

\[ \Delta \nu = \frac{2\nu}{C} \sqrt{\frac{2kT}{m}} \ln 2 \approx 7 \times 10^7 \nu \sqrt{\frac{T}{M}} \]
– Mon Feb 18 Presidents day

– Weds: Rayleigh and Raman Scattering

– Weds Feb 27: Projects Part1