

Fundamentals of Fluorescence

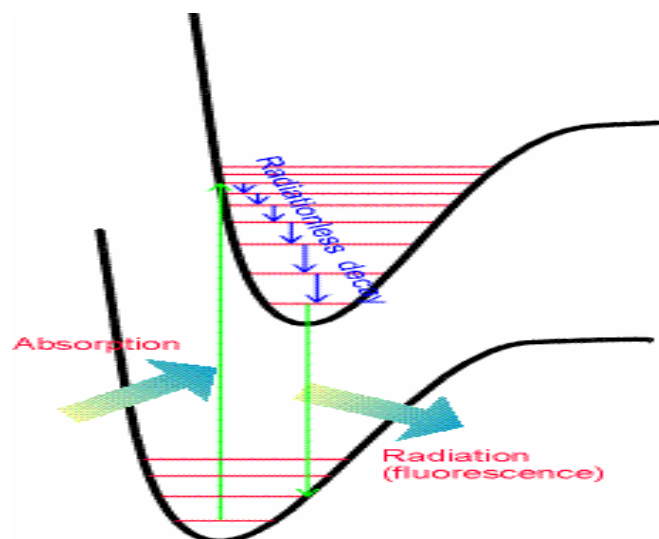


Fig 18. The initial absorption takes the molecule to an excited electronic state. In this state, the molecule is subjected to collisions with the desorbed molecules from the surface and this produces a ladder down to a lower vibrational level. The surrounding molecules may be unable to remove the large energy needed to relax the molecule to the ground electronic state, and it may survive long enough to undergo spontaneous emission, emitting the remaining excess energy as radiation. The downward electronic transition is vertical (in accord with Frank-Condon principle) and the fluorescence spectrum possesses a vibrational structure characteristic of the lower electronic state. The fluorescence occurs at a lower frequency than the incident light: the radiation occurs after some vibrational energy has been discarded into the surroundings.

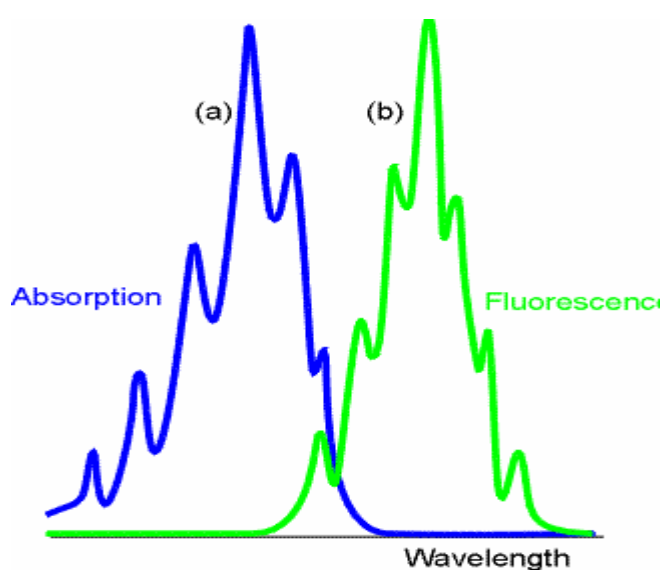


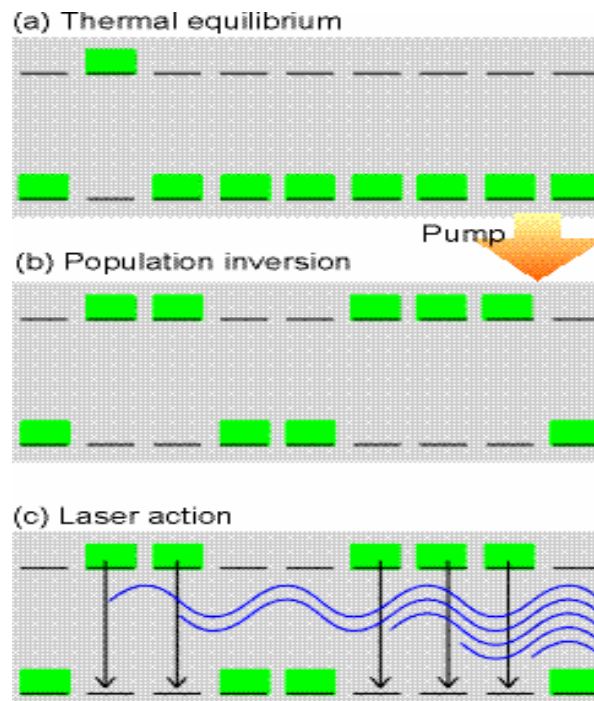
Fig 19

- a) The absorption spectrum shows a vibrational structure characteristic of the upper state.
- b) The fluorescence spectrum shows a structure characteristic of the lower state; it is also displaced to lower frequencies (but the 0-0 transitions are coincident) and resembles a mirror image of the absorption.

Introduction to laser action

Laser action, as the acronym light amplification by stimulated emission of radiation suggests, depends on emission by a stimulated process.

Laser action is schematically, fig 20



- a) Equilibrium population: The Boltzmann population of states, with more atoms in the ground state.
- b) Inverted population: When the initial states absorb, the populations are inverted (the atoms are pumped to the excited state)
- c) Laser action: A cascade of radiation then occurs, as one emitted photon stimulates another atom to emit, and so on. The radiation is coherent (phases in step).

By some means a majority of molecules are excited (pumped) into an upper state. The sample is contained in a cavity between two mirrors, and when a molecule emits spontaneously the photon it generates is reflected backwards and forwards between them. Its presence stimulates other molecules to emit, and they add more photons of the same frequency to the cavity, and these stimulate more molecules to emit then the cascade of energy builds up rapidly.

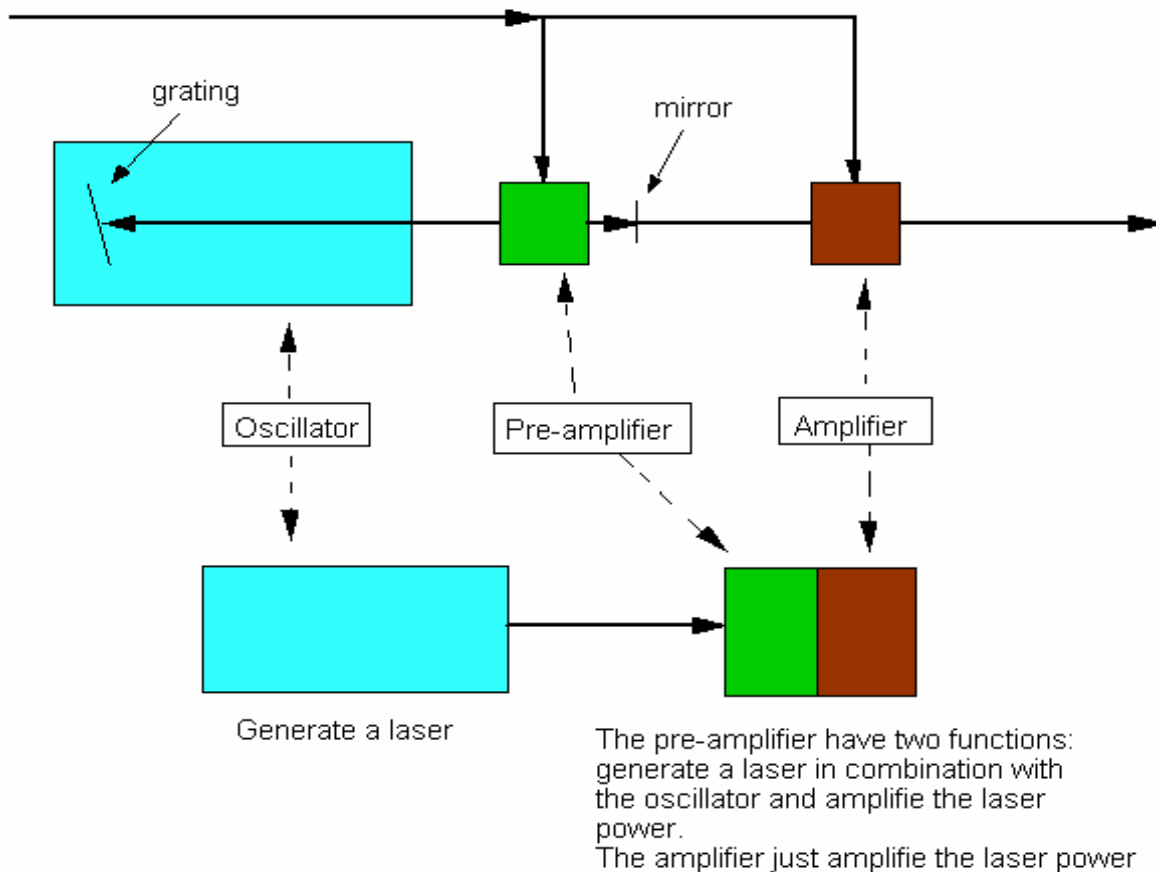
The characteristics of laser light reflect how it is generated: it is monochromatic (because photons stimulate emission of more photons of the same frequency), coherent

(because the phases of the electric fields of the radiation are in step), and non-divergent (because photons travelling at an angle to the cavity axis are not trapped and do not stimulate others).

Excimer and dye Lasers

The excimer laser, A in the picture, generates intense pulses (35-70 nJ) of radiation at wavelengths in the UV region of the spectrum, depending of the operating gas mix, by transition from the excited molecules in a high excited state to a low state.

Dye laser



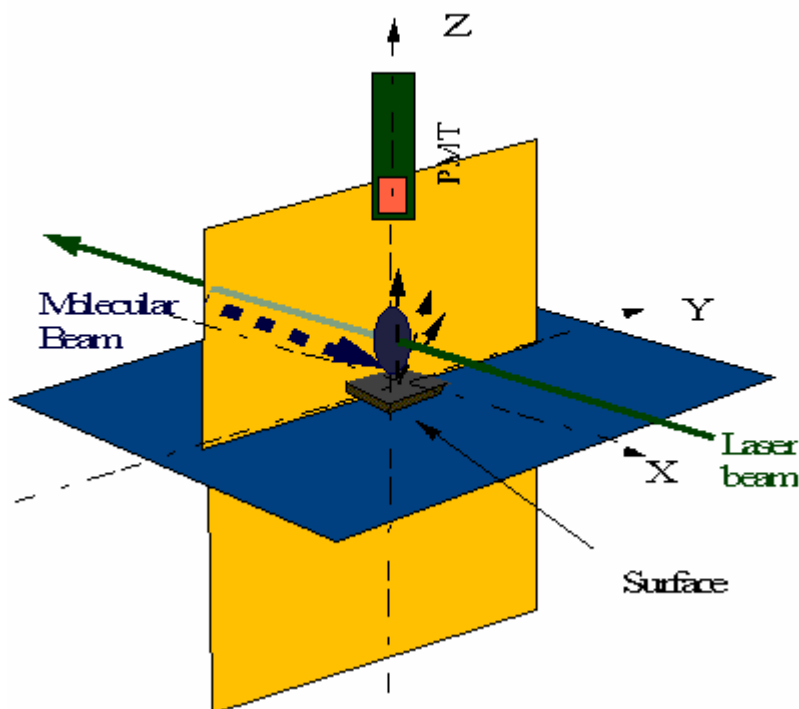
The dye laser, in the picture, is a laser with a tunable wavelength source. The dye laser is pumped by an excimer laser and a weak dye laser is generated in an oscillator, then amplified by the dye laser power amplifiers. Changing the angle of the grating is changed the wavelength of a dye laser.

Laser-Induced Fluorescence

Laser-induced fluorescence (LIF) is the optical emission from molecules that have been excited to higher energy levels by absorption of electromagnetic radiation.

In (LIF), a sample absorbs electromagnetic radiation from a laser and some of its molecules are excited to higher energy levels. Fluorescence is emitted at wavelengths longer than the exciting radiation. Both the absorbed and emitted wavelengths are characteristic of a given molecule.

Schematic layout for LIF measurements



The molecules internal energy distributions (electronic, vibrational, and rotational) can be determined. Therefore energy information before and after scattering of a molecule from a surface can be obtained.

In addition to obtaining internal energy information, the angular distribution can be determined by turning the sample surface, thus scattered molecules are excited by the laser and produce fluorescence detected by a Photomultiplier.

Because the emitted wavelength is different to the exciting wavelength, fluorescence detection is very sensitive relative to absorption measurements. In some cases LIF sensitivities approach the detection of a single atom or molecule, also for molecules that can be resonant excited, LIF provides selective excitation of the sample to avoid interferences.

The LIF spectrum has two forms: Low resolution spectra and high-resolution spectra.

Low-resolution spectra

The peak signal height of each vibration bandhead is measured, divided by the Franck-Condon factor for the absorption and further divided by the laser photon flux at the excitation wavelength (measured relative to the peak flux of the dye range). If the intensity of emission for any upper vibrational state is assumed to be constant, this directly yields the relative vibrational populations if the variation of emission probability with transitions frequency is assumed to be negligible.

T_{vib} , characteristic vibrational temperature is obtained from the assumption that the relative vibrational populations follow the Boltzmann equation:

$$N(v'') \propto \exp(-E_{\text{vib}}/kT_{\text{vib}})$$

Where $E \cong (v'' + \frac{1}{2})\omega_e hc$ to a first approximation

Hence: $\ln(N(v'')) = -(v'' + \frac{1}{2})\omega_e hc/kT_{\text{vib}}$

Therefore, a plot of $\ln(N(v''))$ vs. $(v'' + \frac{1}{2})$ yields a gradient of $\omega_e hc/kT_{\text{vib}}$, giving a value for T_{vib} .

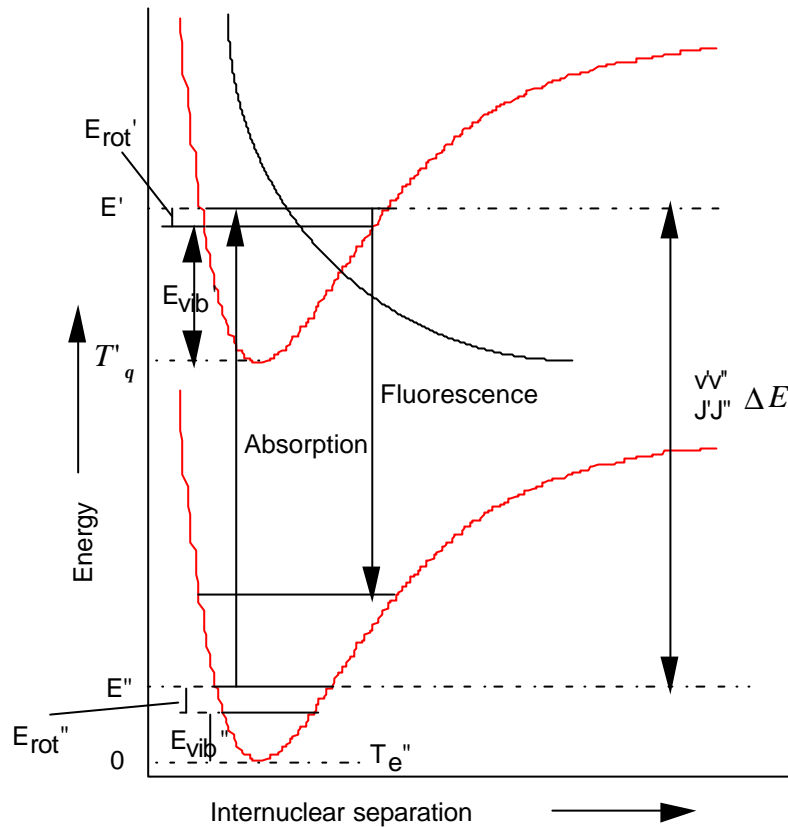
High-resolution spectra

Well isolated P and R branch rotational pairs occur for high rotational quantum (J) numbers for same vibrational bands which are sufficiently separated to prevent overlap at these high J values.

In scattering experiments the molecules are not in thermal equilibrium so they are not characterized by T_{vib} and T_{rot} . The LIF spectra are used to find the initial lower state vibrational and rotational population.

Energy gap, wavelength and frequency of transitions

To deduce the energy difference between defined vibrotational states in the ground and excited electronic states the energies of the electronic, vibrational and rotational modes of the molecules must be considered



Typical form of the potential energy curves for the ground and excited electronic states of a diatomic molecule (the term symbols are applicable to Br_2).

All the energies are referred to the minimum of the ground state potential; so $T_e'' = 0.0$. The vibrational energy, E_{vib} , for any molecule with vibrational quantum number v , referred to the minimum of its potential energy curves is approximately given by the eq.(39) and the rotational energy, E_{rot} , of a molecule with rotational quantum number J , referred to the $J = 0$ level for any vibrational level, is given by the eq.(25) being $E_{\text{vib}} + E_{\text{rot}}$ given in the eq (49).

Hence $E = T_e + E_{\text{vib}} + E_{\text{rot}}$ and the energy difference between defined vibrotational states in the ground and excited electronic states is given by

$$\Delta E = E' - E'' \quad (60)$$

Then substituting and converting units, we have the frequency of the transition, ν , in Hertz

$$\nu = \frac{\nu', \nu''}{J', J''} \Delta E \cdot c \quad (61)$$

where c is the velocity of light in cm.s^{-1} .

Intensity of emission, (I_{pc})

The emission intensity in $J\ s^{-1}$ from a given J' state to any allowed J'' state is given, for an upper state rotational population, $F(v', J')$, as:

$${}_{J'J''}^{v'v''}I_{em} = \frac{K_1 \cdot v^4 \cdot S_e(J', J'') \cdot F(v', J')}{(2J'+1)} \quad (62)$$

Where K_1 is a proportionality constant and $S_e(J', J'')$ is the Honl-London factor for the rotational transition. However the detector signal is photon flux, so we must divide by $h\nu$ dividing:

$${}_{J'J''}^{v'v''}I_{pc} = \frac{K_2 \cdot v^3 \cdot S_e(J', J'') \cdot F(v', J')}{(2J'+1)} \quad (63)$$

The emission also involves a transition in vibrational quantum number, so the Franck-Condon factor, $q_e(v', v'')$ must be also be included:

$${}_{J'J''}^{v'v''}I_{pc} = \frac{K_3 \cdot v^3 \cdot S_e(J', J'') \cdot q_e(v', v'') \cdot F(v', J')}{(2J'+1)} \quad (64)$$

The transitions also involve a change in electronic state. The electronic transition moment is assumed to be independent of vibrational and rotational quantum number, being a constant included in the term K_3 .

The experimental LIF spectrum also depends on the spectral efficiency of the detector, which is a function of wavelength, $D(\lambda_{em})$.

Then, in general, the relative photon count rate, $\langle I_{pc} \rangle$, is a summation of the above equation over all allowed values of v'' and J'' in emission, without the proportionality constant:

$$\langle I_{pc} \rangle = \sum_{\substack{\text{all-}v'' \\ \text{all-allowed-}J''}} \frac{v^3 \cdot S_e(J', J'') \cdot q_e(v', v'') \cdot F(v', J') \cdot D(\lambda_{em})}{(2J'+1)} \quad (65)$$

Population, $F(v', J')$

The population, $F(v', J')$ is determined by the absorption process, which occur from the ground state to this state. This population is proportional to the laser photon flux at the absorbing wavelength, $\phi(\lambda_{abs})$, the relative population of the ground state, $F_{ini}(v'', J'')$,

the Franck-Condon factor for the absorption, $q_a(v'',v')$, and the Honl-London factor for the rotational absorption, $S_a(J'',J')$.

Then:

$$\frac{v''v'}{J''J'} I_{\text{flux}} = \frac{K \cdot S_a(J'',J') \cdot q_e(v'',v') \cdot F_{\text{ini}}(v'',J'') \cdot \phi(\lambda_{\text{abs}})}{(2J'+1)} \quad (66)$$

The electronic transition probability is assumed to be a constant, independent of the vibrational and rotational quantum numbers, and hence is included in the factor K.

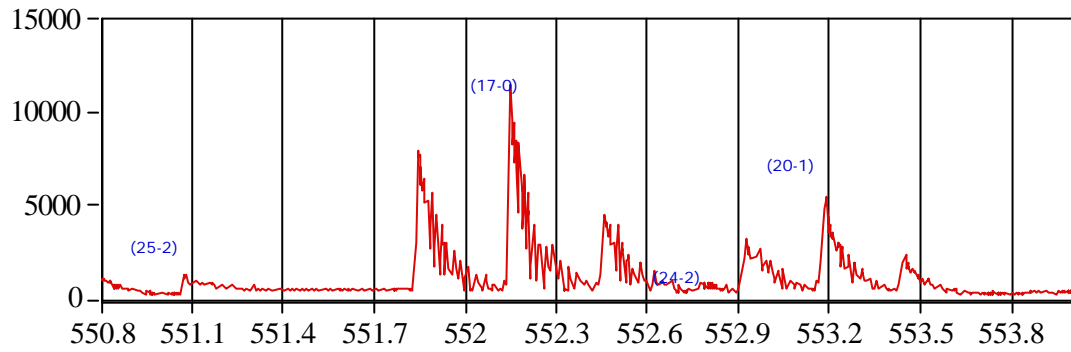
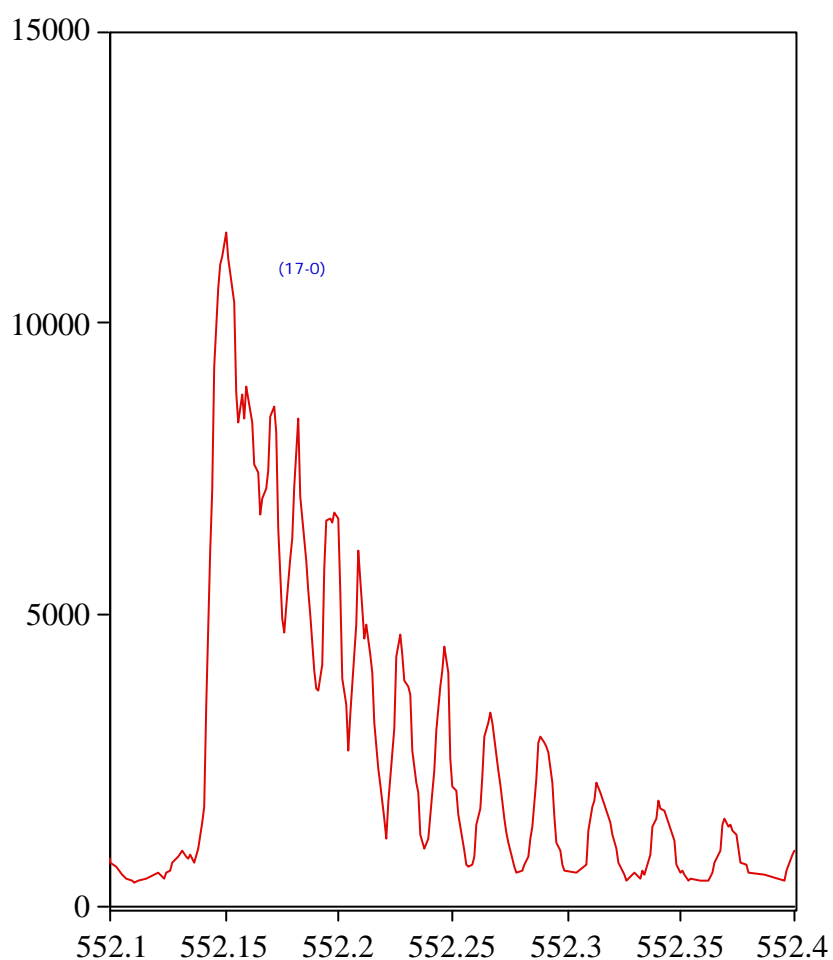


Fig 1 shows a typical LIF spectrum for Br_2 . The different peaks are the transitions of LIF between a vibrational level, $v''=0$ of the ground electronic level, $X^1\Sigma_g^+$ to vibrational level, $v'=17$ of the excited electronic level, $B^3\Pi_{ou}^+$, in the case of the (17-0) transition. As we can see, for example (17-0) transition, we have three large peaks. Each one is due to a different isotope mixture of Br_2 , $^{79}\text{Br}^{79}\text{Br}$, $^{79}\text{Br}^{81}\text{Br}$ and $^{81}\text{Br}^{81}\text{Br}$. The isotope abundance ratio is 1:2:1. We are interested in the $^{79}\text{Br}^{81}\text{Br}$, the biggest one in this case. If we have a look at of a particular vibrational level, we see, fig 2:



This rotationally resolved spectrum is for the transition from the vibrational level, $v''=0$ into a ground electronic level, $X^1\Sigma_g^+$ to the vibrational level, $v'=17$, into an excited electronic level, $B^3\Pi_{ou}^+$, of Br_2 . The x-axis is the wavelength, λ , and the y-axis is the intensity of the fluorescence. In this picture we can see with more detail the different rotational level associated with a particular vibrational level.