Deflected Talbot mediated overtone spectroscopy in near-infrared as a label-free sensor on a chip - Supporting Information

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Oscillator strength of overtones and fundamental modes

The probability of a transition is expressed by the oscillator strength. The oscillator strength is proportional to the square of electric dipole transition moment:

$$f = \left(\frac{4\pi m_e \nu_{ij}}{3e^2\hbar}\right) \left|\mu_{ij}\right|^2 \tag{S-1}$$

where m_e is the mass of an electron, \hbar is the reduced Planck constant, ν_{ij} is the frequency for transition from state *i* to state *j* and μ_{ij} is the electric dipole transition moment which is defined as:

$$\mu_{ij} = \langle i|\mu|j \rangle = \int \psi_i \mu \psi_j \, dr \tag{S-2}$$

where ψ is the wave function, and μ is the electric dipole moment which is defined as:

$$\mu = \mu_0 + \left(\frac{\partial\mu}{\partial r}\right)_0 r + \frac{1}{2} \left(\frac{\partial^2\mu}{\partial r^2}\right)_0 r^2 + \dots$$
 (S-3)

where μ_0 is the dipole moment at r = 0 where r is the displacement and 0 indicates that the derivatives are at the equilibrium bond length.

When $i \neq j$ the states are orthogonal to each other. Hence, the electric dipole transition moment is

$$< i|\mu|j > = \left(\frac{\partial\mu}{\partial r}\right)_{0} < i|r|j >$$

$$+ \frac{1}{2} \left(\frac{\partial^{2}\mu}{\partial r^{2}}\right)_{0} < i|r^{2}|j > + \dots$$
(S-4)

However, a molecule has electrical and mechanical anharmonicity that causes a molecule to behave as an anharmonic oscillator. The vibrational energy levels of a molecule can be calculated using the time-independent Schrödinger equation which defined as:

$$E\psi = \widehat{H}\psi = (\widehat{T} + \widehat{V})\psi = -\frac{\hbar^2}{2M}\nabla^2\psi + V(r)\psi$$
(S-5)

where E is the total energy, \hbar is the reduced Planck constant, M is the effective mass, V(r) is the potential energy, \hat{H} is the Hamiltonian, which is the operator for the total energy of a system, and \hat{T} and \hat{V} are the operators for the kinetic energy and the potential energy, respectively.

An estimated model for an anharmonic oscillator energy levels is the Morse potential function

$$E(r) = V(r) = D_e (1 - \exp[-a(r - r_e)])^2$$
(S-6)

where D_e is the dissociation energy, a is a constant for a particular molecule, r is the distance between atoms and r_e is the equilibrium bond distance. The energy levels are approximated as:¹

$$E_v = (v+1/2)\hbar\omega - (v+1/2)^2\chi_e\hbar\omega$$
(S-7)

where v is the number of the energy level, \hbar is the reduced Planck constant, χ_e is the anharmonicity coefficient and ω is the angular frequency.

In polyatomic molecules, the vibration affects other bonds and the restoring force where more than one vibrational displacement is involved. Instead of using the displacement r, we define Q_i , which is the linear combination of the mass-weighted coordinates q_i . For example, for a symmetric stretch of CO₂, the linear combination of the displacements Q is defined as:

$$Q = \frac{1}{\sqrt{2}}(q_1 - q_3)$$
(S-8)

where q is the mass-weighted coordinates, which is defined as:

$$q_i = \sqrt{m_i} r_i \tag{S-9}$$

Using the new definition of the displacement, the dipole moment of a diatomic molecule is defined as:

$$\mu = \mu_0 + \sum_i \left(\frac{\partial \mu}{\partial Q_i}\right)_0 Q_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \mu}{\partial Q_i \partial Q_j}\right)_0 Q_i Q_j + \dots$$
(S-10)

Due to the anharmonicity, the higher order derivatives in the dipole moment are non-zero and cannot be neglected. Therefore, the probability of transitions of $\Delta v > 1$ (for example: $0\rightarrow 1, 0\rightarrow 2$ and $0\rightarrow 3$) is non-zero and the transitions are allowed. The transition of $\Delta v > 1$ is called overtone.

Evolution of guided mode

We studied the evolution of the guided modes in the waveguides with inclusions as presented in the manuscript. Using Lumerical - FDTD software, we modeled the waveguide when the inclusions are embedded in different media: air and weakly absorbing media of Nmethylaniline molecule. A Gaussian beam, with wavelength of 1.5 μ m, radius of 4.75 μ m and divergence angle of 0.13 rad, was launched into the waveguide. The inclusions were engraved at a distance of 20 μ m from the input facet. Cross-sections in y-z plane were placed at a distance of 15.5-28.25 μm with an interval of 0.75 μm from the input of the waveguide. Figure S-1 shows cross-sections of the guided mode of the rib waveguide in air which experiences multimode interference due Talbot effect. Figure S-2 shows cross-sections of the guided mode of the rib waveguide in N-methylaniline. The change in the superstrate from air to N-methylaniline, increases the refractive index and affects the beat-length of Talbot effect. As a result, the cross-section of the propagating mode changes. Figure S-3 shows cross-sections of the guided mode of the rib waveguide with inclusions in air. Figure S-4 shows cross-sections of the guided mode of the rib waveguide with inclusions in Nmethylaniline. Figure S-3 and Figure S-4 show that when inclusions are placed in the rib waveguide, Talbot effect is deflected which appear as a change in the evolution of the mode along the propagation direction of the modes.



Figure S-1: Cross-sections of the rib waveguide in air. The location of the cross section is indicated above each subplot.



Figure S-2: Cross-sections of the rib waveguide in N-methylaniline. The location of the cross section is indicated above each subplot.



Figure S-3: Cross-sections of the rib waveguide with inclusions in air. The location of the cross section is indicated above each subplot.



Figure S-4: Cross-sections of the rib waveguide with inclusions in *N*-methylaniline. The location of the cross section is indicated above each subplot.

References

 Atkins, P. W.; Friedman, R. S. Molecular quantum mechanics; Oxford university press, 2011.