

Appendix A

Calculation of absorption spectra by time-dependent methods

The following derivations are presented here for reasons of self-consistency of this thesis. Original derivations have been given in the literature, using, in part, different notations, *e.g.* Heller [65].

A.1 Derivation of a microscopic expression for the absorption cross section using time dependent perturbation theory

The intensity I (energy crossing through a unit area per unit time) of a light beam passing in z -direction through a gas of molecules which absorbs electromagnetic energy and converts it into internal (for example vibrational) energy decreases according to Beer's law [41],

$$I(z) = I_0 \cdot e^{-\sigma(\omega)\rho z}. \quad (\text{A.1})$$

In equation (A.1), ρ is the density (number of molecules per volume) and $\sigma(\omega)$ is the molecule-characteristic and frequency- (but not intensity-) dependent absorption cross section.

For the derivation of the theoretical absorption cross section by time-dependent perturbation theory we start with the one-dimensional time-dependent Schrödinger equation in the Born-Oppenheimer approximation:

$$i\hbar \frac{\partial}{\partial t} \chi_l^{vib}(q_a, t) = \underbrace{\left(-\frac{\hbar^2}{2\mu_a} \frac{\partial^2}{\partial q_a^2} + V_l(q_a) \right)}_{= H_0} \chi_l^{vib}(q_a, t) - \underbrace{\epsilon(t) \cdot \sum_j \underline{\mu}_{lj}(q_a)}_{= +\lambda \hat{W}(t)} \cdot \chi_j^{vib}(q_a, t), \quad (\text{A.2})$$

In equation (A.2) the interaction with the electric field is described within the electric dipole approximation. The real dimensionless parameter λ is much smaller than one to assure a small perturbation by the electric field $\hat{W}(t)$ in comparison with the unperturbed Hamiltonian H_0 .

In the case of the time-independent Hamiltonian H_0 , the formal solution of the time-dependent Schrödinger equation is

$$\chi_l(t) = e^{-iH(t-t_0)/\hbar} \chi_l(t_0). \quad (\text{A.3})$$

The eigenfunctions of the operator H_0 , $\Theta_{v_l}^{vib}$, with

$$\hat{H}_0 \Theta_{v_l}^{vib} = E_{v_l} \Theta_{v_l}^{vib} \quad (\text{A.4})$$

can be used to expand the time-dependent vibrational nuclear wavefunction $\chi_l^{vib}(t)$:

$$|\chi_l^{vib}(t)\rangle = \sum_{w_l} c_{w_l}(t) |\Theta_{w_l}^{vib}\rangle, \quad (\text{A.5})$$

where

$$c_{w_l}(t) = \langle \Theta_{w_l}^{vib} | \chi_l^{vib}(t) \rangle. \quad (\text{A.6})$$

Expansion (A.5) holds for a discrete and complete eigenbasis:

$$\sum_{v_l} |\Theta_{v_l}^{vib}\rangle \langle \Theta_{v_l}^{vib}| = \underline{1}. \quad (\text{A.7})$$

Only bound-bound transitions are considered in this section. A generalization to bound-free transitions is given by Schinke [41]. Multiplication on the left with $\langle \Theta_{v_l}^{vib} |$ yields (index q_a denotes an integration over q_a in coordinate space):

$$i\hbar \frac{\partial}{\partial t} c_{v_l}(t) = E_{v_l} \cdot c_{v_l}(t) + \lambda \cdot \sum_j \sum_{w_j} c_{w_j}(t) \langle \Theta_{v_l}^{vib} | \left(-\epsilon(t) \underline{\mu}_{lj} \right) | \Theta_{w_j}^{vib} \rangle_{q_a}. \quad (\text{A.8})$$

An electronic two-level system is assumed where the initial (i) state ($j = i$) (e.g. the electronic ground state) is coupled with only one final (f) state ($l = f$) (e.g. an electronic excited state) by an electric field. The time-dependent equation for the final state f reads then as:

$$i\hbar \frac{\partial}{\partial t} c_{v_f}(t) = E_{v_f} \cdot c_{v_f}(t) + \lambda \cdot \sum_{w_i} c_{w_i}(t) \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}(t) \cdot \underline{\mu}_{fi} \right) | \Theta_{w_i}^{vib} \rangle_{q_a}, \quad (\text{A.9})$$

where $\underline{\mu}_{fi}$ is the transition dipole moment that connects the initial (i) with the final (f) state. In the absence of the electric field ($\lambda = 0$) the solution of the last equation is very simple:

$$c_{v_f}(t) = b_{v_f}(t_0) e^{-iE_{v_f}(t-t_0)/\hbar}. \quad (\text{A.10})$$

With this solution equation (A.5) becomes

$$|\chi_f(t)\rangle = \sum_{v_f} c_{v_f}(t_0) e^{-iE_{v_f}(t-t_0)/\hbar} |\Theta_{v_f}^{vib}\rangle \quad (\text{A.11})$$

which is a coherent superposition of eigenstates (*i.e.* a wavepacket). Substituting (A.11) into (A.3), one obtains

$$\begin{aligned} \sum_{v_f} c_{v_f}(t_0) e^{-iE_{v_f}(t-t_0)/\hbar} |\Theta_{v_f}^{vib}\rangle &= e^{-i\hat{H}(t-t_0)/\hbar} \underbrace{\sum_{v_f} c_{v_f}(t_0) \underbrace{e^{-iE_{v_f}(t_0-t_0)/\hbar}}_{=1} |\Theta_{v_f}^{vib}\rangle}_{\chi_f(t_0)} \\ &= e^{-i\hat{H}(t-t_0)/\hbar} \sum_{v_f} c_{v_f}(t_0) |\Theta_{v_f}^{vib}\rangle. \end{aligned} \quad (\text{A.12})$$

This means that the propagator $e^{-i\hat{H}(t-t_0)/\hbar}$ can be replaced by the relative phase factors $e^{-iE_{v_f}(t_0-t_0)/\hbar}$. Only if the initial state is an eigenstate (e.g. $c_{w_f} = 1$, $c_{v_f} = 0$ for $w_f \neq v_f$) the time evolution is described by a global phase factor, $e^{-i\hat{H}(t-t_0)/\hbar} = e^{-iE_{w_f}(t-t_0)/\hbar}$, with no physical importance.

If the perturbation by the electric field is small, the solution of equation (A.9) is close to solution (A.10), i. e. the solution in the unperturbed case. The solution for small perturbations can be predicted to be

$$c_{v_f}(t) = b_{v_f}(t) e^{-\frac{i}{\hbar} E_{v_f} t}, \quad (\text{A.13})$$

where in opposition to equation (A.10) the coefficient $b_{v_f}(t)$ is a function of time. Substituting (A.13) into (A.9), one obtains:

$$i\hbar \cdot e^{-\frac{i}{\hbar} E_{v_f} t} \cdot \frac{\partial}{\partial t} b_{v_f}(t) + \underbrace{i\hbar \cdot b_{v_f}(t) \cdot \frac{\partial}{\partial t} e^{-\frac{i}{\hbar} E_{v_f} t}}_{=E_{v_f} b_{v_f}(t) e^{-\frac{i}{\hbar} E_{v_f} t}}$$

$$= E_{v_f} b_{v_f}(t) e^{-\frac{i}{\hbar} E_{v_f} t} + \lambda \cdot \sum_{w_i} \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i} \right) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot b_{w_i}(t) \cdot e^{-\frac{i}{\hbar} E_{w_i} t}. \quad (\text{A.14})$$

Multiplying both sides of the last equation by $e^{+\frac{i}{\hbar} E_{v_f} t}$ leads to:

$$i\hbar \frac{\partial}{\partial t} b_{v_f}(t) = \lambda \cdot \sum_{w_i} b_{w_i}(t) \cdot \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i} \right) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar} (E_{v_f} - E_{w_i}) t}. \quad (\text{A.15})$$

For $t < 0$ the system is assumed to be represented by the vibrational eigenfunction $\Theta_{w_i=i_i}^{vib}$ (e.g. the vibrational ground state ($i_i = 0$) of the electronic ground state ($i = 0$)). The only non-vanishing coefficient is $b_{w_i=i_i}(t < 0) = 1$ which is independent of time, since there is no perturbation of the system:

$$b_{w_i=i_i}(t < 0) = 1, \quad b_{w_i}(t < 0) = 0 \text{ else,}$$

$$\text{and } b_{v_f}(t < 0) = 0, \quad (\text{A.16})$$

and therefore:

$$\chi_i(t < 0) = \Theta_{w_i}^{vib}$$

$$\chi_f(t < 0) = 0. \quad (\text{A.17})$$

For $t \geq 0$ equation (A.15) may be solved by first-order perturbation theory [51]. As the perturbation is increased from zero to a finite value, the new energy and wave function must also change continuously, and they can be written as a Taylor expansion in powers of the perturbation parameter λ .

$$b_n(t) = \lambda^0 \cdot b_n^{(0)}(t) + \lambda^1 \cdot b_n^{(1)}(t) + \lambda^2 \cdot b_n^{(2)}(t) + \dots \quad (\text{A.18})$$

Substituting this expansion into (A.15), one obtains:

$$\lambda^0 \cdot i\hbar \frac{\partial}{\partial t} b_{v_f}^{(0)}(t) + \lambda^1 \cdot i\hbar \frac{\partial}{\partial t} b_{v_f}^{(1)}(t) + \lambda^2 \cdot i\hbar \frac{\partial}{\partial t} b_{v_f}^{(2)}(t) + \dots = \quad (\text{A.19})$$

$$\lambda \cdot \lambda^0 \cdot \sum_{w_i} b_{w_i}^{(0)}(t) \cdot \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i} \right) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar} (E_{v_f} - E_{w_i}) t} +$$

$$\lambda \cdot \lambda^1 \cdot \sum_{w_i} b_{w_i}^{(1)}(t) \cdot \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i} \right) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar} (E_{v_f} - E_{w_i}) t} +$$

$$\lambda \cdot \lambda^2 \cdot \sum_{w_i} b_{w_i}^{(1)}(t) \cdot \langle \Theta_{v_f}^{vib} | (-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i}) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar}(E_{v_f} - E_{w_i})t} + \dots \quad (\text{A.20})$$

Collecting terms with the same power of λ gives:

$$\lambda^0 (r = 0) : i\hbar \frac{\partial}{\partial t} b_{v_f}^{(0)}(t) = 0$$

$$\lambda^1 (r = 1) : i\hbar \frac{\partial}{\partial t} b_{v_f}^{(1)}(t) = \sum_{w_i} b_{w_i}^{(0)}(t) \cdot \langle \Theta_{v_f}^{vib} | (-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i}) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar}(E_{v_f} - E_{w_i})t}$$

⋮

$$\lambda^n (r = n) : i\hbar \frac{\partial}{\partial t} b_{v_f}^{(r)}(t) = \sum_{w_i} b_{w_i}^{(r-1)}(t) \cdot \langle \Theta_{v_f}^{vib} | (-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i}) | \Theta_{w_i}^{vib} \rangle_{q_a} \cdot e^{\frac{i}{\hbar}(E_{v_f} - E_{w_i})t}$$

The zeroth-order ($r=0$) solution for $t \geq 0$ is identical with the initial conditions (A.16):

$$b_{w_i=i_i}(t \geq 0) = 1, \quad b_{w_i}(t \geq 0) = 0 \text{ else,}$$

$$\text{and } b_{v_f}(t \geq 0) = 0. \quad (\text{A.21})$$

This result permits one to write the first-order ($r=1$) solution in the form:

$$i\hbar \frac{\partial}{\partial t} b_{v_f}(t) = \langle \Theta_{v_f}^{vib} | (-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i}) | \Theta_{i_i}^{vib} \rangle_{q_a} \cdot e^{it \cdot \omega_{v_f i_i}}, \quad (\text{A.22})$$

where

$$\omega_{v_f i_i} = \frac{(E_{v_f} - E_{i_i})}{\hbar} \quad (\text{A.23})$$

is the transition frequency (Bohr frequency). The first-order solution is valid for small coupling elements or more precisely, if

$$\frac{\hbar}{|\langle \Theta_{v_f}^{vib} | (-\underline{\epsilon}(t) \cdot \underline{\mu}_{f_i}) | \Theta_{i_i}^{vib} \rangle_{q_a}|} \gg t, \quad (\text{A.24})$$

where t is the time duration of the perturbation. Within this approximation it is explicitly assumed that the populations of the initial and the final state do not significantly change while the light beam is switched on, i. e. (A.21) holds approximately. If the electric field is described by a cosine-function,

$$\underline{\epsilon}(t) = \epsilon_0 \underline{e} \cdot \cos(\omega t) = \underline{\epsilon}_0 \cdot \cos(\omega t), \quad (\text{A.25})$$

with $\epsilon_0 = |\underline{\epsilon}_0|$ and \underline{e} being the unit vector in the direction of the electric field, one obtains:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} b_{v_f}(t) &= \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}_0 \cdot \underline{\mu}_{f_i} \right) | \Theta_{i_i}^{vib} \rangle_{q_a} \cdot e^{i\omega_{v_f i_i} t} \cdot \cos(\omega t) \\ &= W_{v_f i_i} \cdot e^{i\omega_{v_f i_i} t} \cdot \frac{1}{2} (e^{i\omega t} + e^{-i\omega t}), \end{aligned} \quad (\text{A.26})$$

where the shorthand notation

$$W_{v_f i_i} = \langle \Theta_{v_f}^{vib} | \left(-\underline{\epsilon}_0 \cdot \underline{\mu}_{f_i} \right) | \Theta_{i_i}^{vib} \rangle_{q_a} \quad (\text{A.27})$$

was introduced. Integration of (A.26) yields [41]:

$$b_{v_f}(t) = \frac{W_{v_f i_i}}{2\hbar} \cdot \left(\frac{1 - e^{i(\omega_{v_f i_i} + \omega)t}}{\omega_{v_f i_i} + \omega} + \frac{1 - e^{i(\omega_{v_f i_i} - \omega)t}}{\omega_{v_f i_i} - \omega} \right). \quad (\text{A.28})$$

For $\omega \approx \omega_{v_f i_i}$ the second term of (A.28) is dominant¹. The first term can be neglected under the condition that

$$\frac{1}{\omega_{v_f i_i}} \approx \frac{1}{\omega} \propto T^{osc} \ll t, \quad (\text{A.29})$$

T^{osc} being the oscillation period of the electromagnetic field. This is called the rotating wave approximation (RWA) and implies that during the interval $[0, t]$ many oscillations of $\epsilon(t)$ are possible, i. e. $\epsilon(t)$ acts as a cosine-perturbation with a certain oscillation period. Combining conditions (A.24) and (A.29), it follows:

$$\frac{1}{\omega_{v_f i_i}} \ll t \ll \frac{\hbar}{W_{v_f i_i}} \Rightarrow \hbar\omega_{v_f i_i} = E_{v_f} - E_{i_i} \gg W_{v_f i_i}. \quad (\text{A.30})$$

This means that the energy difference $E_{v_f} - E_{i_i}$ must be much larger than the coupling element $W_{v_f i_i}$. If (A.30) is fulfilled, the first-order solution and the rotating wave approximation are valid and the population of the final state can be written as [50, 41]:

$$P_{v_f i_i}(t) = |b_{v_f}(t)|^2 = \left(\frac{W_{v_f i_i}}{\hbar} \right)^2 \cdot \frac{\sin^2[(\omega_{v_f i_i} - \omega) \cdot t/2]}{(\omega_{v_f i_i} - \omega)^2}, \quad (\text{A.31})$$

where the index i_i denotes the dependence of the population of the final state on the initial state i_i . Using

$$\lim_{t \rightarrow \infty} \frac{\sin^2[(\omega_{v_f i_i} - \omega) \cdot t/2]}{(\omega_{v_f i_i} - \omega)^2} = \frac{\pi}{2} \cdot t \cdot \delta(\omega_{v_f i_i} - \omega), \quad (\text{A.32})$$

¹The reverse holds for stimulated emission where $\omega_{v_f i_i} < 0$ [41]. Here, only absorption, $\omega_{v_f i_i} > 0$, is considered.

equation (A.31) reads as

$$P_{v_f i_i}(t) = \left(\frac{W_{v_f i_i}}{\hbar} \right)^2 \cdot \frac{\pi}{2} \cdot t \cdot \delta(\omega_{v_f i_i} - \omega). \quad (\text{A.33})$$

$P_{v_f i_i}(t)$ is sometimes called the transition probability. According to (A.33) it rises linearly with time. The transition rate is defined as the time-derivative of $P_{v_f i_i}(t)$ and therefore is time-independent:

$$k_{v_f i_i} = \frac{d}{dt} P_{v_f i_i} = \left(\frac{W_{v_f i_i}}{\hbar} \right)^2 \cdot \frac{\pi}{2} \cdot \delta(\omega_{v_f i_i} - \omega). \quad (\text{A.34})$$

Equation (A.34) yields the constant transition probability per unit time. The decrease of intensity I of a light beam passing through a gas of absorbing molecules can be written as [41]:

$$\frac{dI}{dz} = -\rho \cdot \underbrace{\frac{2}{\varepsilon_0 c} \hbar \omega_{v_f i_i} \cdot k_{v_f i_i}}_{\sigma(\omega)} \cdot \frac{1}{|\epsilon_0|^2} \cdot I. \quad (\text{A.35})$$

Inserting equation (A.34) into (A.35) leads to the microscopic expression of the phenomenological partial absorption cross section defined in equation (A.1):

$$\sigma_{v_f i_i}(\omega) = \frac{\pi}{\hbar \varepsilon_0 c} \cdot \omega_{v_f i_i} \cdot \delta(\omega_{v_f i_i} - \omega) \cdot |\langle \Theta_{v_f}^{vib} | (-\underline{\mu}_{f_i}^{(e)}) | \Theta_{i_i}^{vib} \rangle_{q_a}|^2, \quad (\text{A.36})$$

where $\underline{\mu}_{f_i}^{(e)} = \underline{e} \cdot \underline{\mu}_{f_i}$ denotes the transition dipole moment in the direction of the electric field (unit vector \underline{e}). The cross section defined in equation (A.36) is an example of the *Fermi's Golden Rule*. The total absorption cross section resulting from excitation to the electronic state f is just the sum of the individual partial cross sections of different vibrational levels v_f :

$$\sigma_{f i_i}^{tot}(\omega) = \sum_{v_f} \sigma_{v_f i_i}(\omega). \quad (\text{A.37})$$

If more than one excited (final) state is involved, the absorption spectrum results from the summation over all electronic states:

$$\sigma_{i_i}^{tot}(\omega) = \sum_f \sigma_{f i_i}^{tot}(\omega). \quad (\text{A.38})$$

A.2 Time-dependent calculation of the absorption cross section: The autocorrelation function

The aim of this section is to show how the absorption spectrum can be calculated using time-dependent wavepackets. The central quantity in this business is the autocorrelation function which will be defined below.

According to (A.36) and (A.37) the total absorption cross section of a final electronic state f is given by

$$\sigma_{f i_i}^{tot}(\omega) = \sum_{v_f} \sigma_{v_f i_i}(\omega) = \sum_{v_f} \frac{\pi}{\hbar \varepsilon_0 c} \cdot \omega_{v_f i_i} |\langle \Theta_{v_f}^{vib} | \left(-\underline{\mu}_{f i}^{(e)} \right) | \Theta_{i_i}^{vib} \rangle_{q_a}|^2 \cdot \delta(\omega_{v_f i_i} - \omega) \quad (\text{A.39})$$

In the first step of the derivation we use the symmetry of the Dirac's δ -function,

$$\delta(\omega_{v_f i_i} - \omega) = \delta(\underbrace{\omega_{i_i} + \omega}_{\omega'} - \omega_{v_f}),$$

and the possibility to write it as

$$\delta(\omega' - \omega_{v_f}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt e^{it(\omega' - \omega_{v_f})}. \quad (\text{A.40})$$

Substituting this into equation (A.39), one gets

$$\sigma_{f i_i}^{tot}(\omega) = \underbrace{\frac{\pi}{\hbar \varepsilon_0 c} \cdot \frac{1}{2\pi} \frac{1}{\hbar}}_{=const} \cdot \int_{-\infty}^{+\infty} dt \sum_{v_f} \underbrace{E_{photon}}_{=\hbar(\omega_{v_f} - \omega_{i_i})} \cdot \langle \Theta_{i_i}^{vib} | \left(-\underline{\mu}_{f i}^{(e)} \right) | \Theta_{v_f}^{vib} \rangle_{q_a} e^{-itE_{v_f}/\hbar} \langle \Theta_{v_f}^{vib} | \left(-\underline{\mu}_{f i}^{(e)} \right) | \Theta_{i_i}^{vib} \rangle_{q_a} \cdot e^{i\omega' t}. \quad (\text{A.41})$$

Using expressions (A.7) and (A.12), equation (A.41) becomes

$$\sigma_{f i_i}^{tot}(\omega) = const \cdot E_{photon} \cdot \int_{-\infty}^{+\infty} dt \underbrace{\langle \left(-\underline{\mu}_{f i}^{(e)} \right) \Theta_{i_i}^{vib} |}_{\langle \chi_f^{vib}(0) |} e^{-\frac{i}{\hbar} \hat{H} t} \underbrace{| \left(-\underline{\mu}_{f i}^{(e)} \right) \Theta_{i_i}^{vib} \rangle_{q_a}}_{| \chi_f^{vib}(t) \rangle} \cdot e^{i\omega' t}. \quad (\text{A.42})$$

The essential step for the calculation of the absorption spectrum by wavepacket propagations is the following ansatz for the initial wavefunction in the excited state f ;

$$| \chi_f^{vib}(0) \rangle = | \mu_{f i}^{(e)} \Theta_{i_i} \rangle. \quad (\text{A.43})$$

The autocorrelation function is defined as

$$S_f(t) = \langle \chi_f^{vib}(0) | \chi_f^{vib}(t) \rangle_{q_a}. \quad (\text{A.44})$$

Finally, substituting this definition into (A.42) yields:

$$\sigma_{f i_i}^{tot}(\omega) = const \cdot E_{photon} \cdot \int_{-\infty}^{+\infty} dt S_f(t) \cdot e^{i\omega' t} = const \cdot E_{photon} \cdot FT(S_f(t)). \quad (\text{A.45})$$

Therefore, the total absorption cross section, $\sigma_{fi}^{tot}(\omega)$, equals (except for a constant factor) the Fourier Transformation (FT) of the autocorrelation function $S_f(t)$. In practice, the initial wavepacket (A.43) is propagated and the autocorrelation function is calculated according to equation (A.44). The spectrum is then obtained by the Fourier Transformation of the autocorrelation function (cf equation (A.45)). The initial condition (A.43) implies a spontaneous excitation (δ -pulse): The initial ($t=0$) excited state wavefunction equals the wavefunction of the vibrational ground state ($v = 0$) of the electronic ground state ($i = 0$) multiplied by the transition dipole function in the direction (\underline{e}) of the electric field, $\mu_{f0}^{(e)}$.

Spectrum in the case of bound-bound transitions

Here, a transition from the bound ground state to a bound excited state f is considered. The initial wavepacket (A.43) at $t = t_0 = 0$ is real and can be written as a linear combination of the (real) eigenfunctions:

$$\chi_f(t_0 = 0) = \sum_{w_f} c_{w_f}(t_0 = 0) \Theta_{v_f}^{vib}(q_a) \quad (\text{A.46})$$

The discrete eigenfunctions and values are defined by equation (A.4) and the completeness relation (A.7) holds. Using the wavepacket equation (A.11) for $t = t_0 = 0$ and $t = t$, the expression (A.44) of the autocorrelation function results in

$$\begin{aligned} S(t) &= \int d_{q_a} \left(\sum_{w_f} c_{w_f}^*(t_0 = 0) (\Theta_{v_f}^{vib}(q_a))^* \right) \cdot \left(\sum_{v_f} c_{v_f}(t_0 = 0) e^{-iE_{v_f}t/\hbar} \Theta_{v_f}^{vib}(q_a) \right) \\ &= \sum_{v_f} |c_{v_f}(0)|^2 e^{-iE_{v_f}t/\hbar} \end{aligned} \quad (\text{A.47})$$

From the last expression it is obvious that the autocorrelation fulfills the symmetry relation

$$S(-t) = S^*(t) \quad (\text{A.48})$$

which guarantees that the absorption spectrum (A.45) is real. This is a consequence of the fact that the initial wavepacket (A.43) is real. Propagating till the autocorrelation function is essentially zero, assures that the calculated absorption cross section is positive [41].

According to equation (A.45) the resulting absorption spectrum is

$$\begin{aligned} \sigma_{fi}^{tot}(\omega) &= const \cdot E_{photon} \cdot \int_{-\infty}^{+\infty} dt \sum_{v_f} |c_{v_f}(0)|^2 e^{-iE_{v_f}t/\hbar} \cdot e^{iEt/\hbar} \\ &= const \cdot E_{photon} \cdot \sum_{v_f} |c_{v_f}(0)|^2 \int_{-\infty}^{+\infty} dt e^{i(E-E_{v_f})t/\hbar} \end{aligned}$$

$$= const \cdot E_{photon} \cdot \sum_{v_f} |c_{v_f}(0)|^2 \cdot \frac{2\pi}{\hbar} \delta(E - E_{v_f}), \quad (\text{A.49})$$

where definition (A.40) of the δ -function was applied. Therefore, the absorption spectrum consists of discrete lines with energy E_{v_f} and a height proportional to $|c_{v_f}(0)|^2$. In the case where μ_{fi} is a constant (*Condon approximation*), the $|c_{v_f}(t)|^2$ are equal to $|\mu_{fi}|^2$ times the so-called Franck-Condon factors. The result (A.49) (except for a factor) can be also achieved by a population analysis of the initial wavefunction (if the eigenfunctions and values are known).

Problem of light vs. molecule orientation

Normally the molecule is not oriented and it has to be classically averaged over the different laser polarizations which implies a calculation of three spectra for x-, y- and z-polarized light:

$$\sigma_{fi}^{tot} = \frac{1}{3} \sigma_{fi}^{tot}(x) + \frac{1}{3} \sigma_{fi}^{tot}(y) + \frac{1}{3} \sigma_{fi}^{tot}(z). \quad (\text{A.50})$$

If, however, there is only one dominant component of the transition dipole moment in the Franck-Condon window (e.g. $\mu_{fi,x} \gg \mu_{fi,y/z}$), the transition dipole moment function can be replaced by its modulus at the Franck-Condon point (because the modulus is approximately equal to the dominant component).

$$|\mu_{fi}| = \sqrt{\mu_{f0,x}^2 + \mu_{f0,y}^2 + \mu_{f0,z}^2} \quad (\text{A.51})$$

Using a constant factor instead of the transition dipole moment function is known as the *Condon approximation*.

If more than one electronic excited (final) state is involved, then, according to equation (A.38), the spectrum equals the sum of the individual spectra of the states f :

$$\begin{aligned} \sigma_{ii}^{tot}(\omega) &= \sum_f \sigma_{fi}^{tot}(\omega) = \sum_f const \cdot E_{photon} \cdot \int_{-\infty}^{+\infty} dt S_f(t) \cdot e^{i\omega't} = \\ &const \cdot E_{photon} \cdot \int_{-\infty}^{+\infty} dt \underbrace{\sum_f (S_f(t))}_{S_{tot}(t)} \cdot e^{i\omega't} = const \cdot E_{photon} \cdot FT \left(\sum_f (S_f(t)) \right), \end{aligned} \quad (\text{A.52})$$

where $\hbar\omega' = E_{ii} + \hbar\omega$. This means that in the case of several final electronic states the Fourier Transformation (FT) of the sum of the individual autocorrelation functions, $S_{tot}(t) = \sum_f (S_f(t))$ leads to the total electronic absorption spectrum.