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Molecular photodissociation dynamics: The time-dependent formulation

Niels Engholm Henriksen

Chemistry Laboratory III, H. C. Ørsted Institute, University of Copenhagen,
DK-2100 Copenhagen, Denmark

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Summary. The time-dependent formulation for nuclear dynamics in molecules induced by electronic excitation in a radiation field is reviewed. The present discussion is especially aiming at extracting physical observables for photodissociation and highlighting the connection to the nuclear dynamics of the process. The total dissociation probability, the probability associated with the formation of a given chemical product, and the probability that this product shows up in a specified quantum state is considered. The results are given as a function of the form of the light pulse, and special attention is given to situations where the duration of the light pulse is very short or very long.

Key words: Dynamics – Radiation – Photodissociation

1. Introduction

The time-dependent formulation for nuclear dynamics induced by electronic excitation in a radiation field was introduced more than a decade ago [1]. This description gives the exact quantum mechanical counterpart of the Franck–Condon principle – a qualitative picture which states that at the completion of an electronic transition in a molecule the nuclei are still in their original positions, only after this excitation the nuclei will readjust, i.e., nuclear dynamics will ensue. Furthermore, the time-dependent formulation [1] gives theoretical expressions for observables which can be formulated in such a way that the simple picture associated with the Franck–Condon principle shows up in the equations. These results are based on a theoretical description which use standard theory – wave functions which assumes an adiabatic separation between electronic and nuclear motion and first order perturbation theory for the light-matter interaction.

After the publication of the paper by Kulander and Heller [1] many papers have used and expanded on the foundation given in that paper (see, e.g., [2–17] and references therein), but the whole field is strongly connected to the pioneering work of E. J. Heller. The time-dependent approach has turned out to be very valuable. This is partly due to the intuitively appealing description which is not provided by standard formulations in terms of stationary states and partly due to the ease of making contact with (semi-)classical descriptions and pictures. In addition, in many situations, computational efficiency is provided by the time-dependent approach.

We present here a detailed review and update on the *basic* theoretical concepts associated with the time-dependent formulation for nuclear dynamics induced by electronic excitation. In the process of doing that, it is hoped that various aspects of the theory will be clarified. The discussion is aiming at photodissociation dynamics – the basic theoretical description of other types of nuclear dynamics due to electronic excitation are, however, closely related. Thus, the theory in Sects. 2 and 3 are, e.g., formally identical to the situation where spectroscopy between two bound electronic states is considered.

Why study photofragmentation?

Photofragmentation is chemical bond breaking due to absorption of radiation. The primary electronic transition in the process takes, typically, place in the ultraviolet or visible region of the spectrum.

There are several good reasons for studying this process. From the *reaction dynamics point of view*, it offers a very good opportunity to study dynamics of chemical bond breaking. In bimolecular collisions, the impact parameter cannot be controlled experimentally. In photofragmentation, on the other hand, the reaction conditions are as well-defined as possible – the initial state is a bound molecule with a well-defined geometry, the initial quantum state can be selected and the energy transferred to the molecule via the photon can be controlled with very high precision using laser light. Thus, photofragmentation offers the best opportunity for a "clean" comparison between theory and experiment.

Furthermore, *photofragmentation is an important chemical reaction* per se. It plays an important role, expecially, in the chemistry of the atmosphere. The most well-known of these reactions is probably the photofragmentation of ozone in the stratosphere:

$$O_3 + \hbar\omega \rightarrow O_2 + O \tag{1}$$

It shields the earth from ultraviolet solar radiation for wavelengths less than about 3000 Å. A number of reactions occur due to pollution of the atmosphere, e.g., photofragmentation of chlorofluorocarbons (CFC gases):

$$CCl_3F + \hbar\omega \rightarrow \cdot CCl_2F + Cl\cdot \tag{2}$$

This reaction can create problems because the chlorine radical will react with ozone to yield oxygen and ClO thereby removing ozone.

What are the questions in photofragmentation?

The photofragmentation of a triatomic molecule contains all the essential features of photofragmentation. For a triatomic molecule, the general situation is:

$$ABC(n) + \hbar\omega \rightarrow \begin{cases} A + BC(m) \\ B + AC(m) \\ C + AB(m) \\ A + B + C \end{cases} \tag{3}$$

where all product states can be accessible simultaneously at a given photon energy $\hbar\omega$. *We want to know exactly what happens in the transition from reactants to products* in Eq. (3). This includes questions like:

(a) Probe the process of bond breaking
Can we learn about the details of the bond breaking from measurements in frequency domain? – can we do measurements in real-time and learn about the dissociation time, i.e., how long it takes to go from the left to the right side in Eq. (3)? What is the effect of changing the characteristics of the light – like changing the frequency and perhaps the duration of the light pulse?

(b) Predict the outcome of the reaction
Can we predict the total probability of the reaction? – can we predict the probability associated with the transformation in Eq. (3), i.e., the probability of transforming the triatomic molecule $ABC(n)$, in a given rotational, vibrational, and electronic state (denoted by n), into a given set of fragments on the right-hand side, again with complete specification of rotational, vibrational, and electronic states (denoted by m) as well as a given magnitude and direction of the relative momentum of the fragments? – can we predict how the excess energy in the photofragments is distributed between the rotational, vibrational, translational, and electronic degrees of freedom?

(c) Test of theoretical approaches
Our intuition about dynamics is strongly connected to classical mechanics – can the dynamics of the process be described by semi-classical mechanics?

The questions above are all related to understanding the dynamics of a naturally occurring process. Another type of question is:

(d) Control of reactions: Selective bond breaking
Can we control the outcome of the reaction and select which product is going to be formed? – how can control be achieved?

We will discuss the answers to questions like these in the sections which follow. Only basic theoretical concepts are considered. Numerical techniques and applications to specific systems are not discussed.

2. Quantum dynamics of molecular photofragmentation

We consider a molecule which interacts with a radiation field. An adequate description can be given by considering the molecule to be described by quantum mechanics and a classical description of the radiation field. We let $|\Psi(t)\rangle$ denote the state vector of our molecule at time t. In the Schrödinger picture, the time evolution is given by [18]:

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = (\hat{H}_M + \hat{H}_I(t))\,|\Psi(t)\rangle \tag{4}$$

where $\hat{H}_M$ is the molecular Hamiltonian given by:

$$\hat{H}_M = \hat{T}_n + \hat{T}_e + V \tag{5}$$

$\hat{T}_n$, $\hat{T}_e$, and V are the kinetic energy of the nuclei, the kinetic energy of the electrons, and Coulomb interaction between all the electrons and nuclei, respectively, and $\hat{H}_I(t)$ is the Hamiltonian for the interaction with the radiation field, which can be expanded in the form [19]:

$$\hat{H}_I(t) = \hat{H}_{ED}(t) + \hat{H}_{EQ}(t) + \hat{H}_{MD}(t) + \cdots \tag{6}$$

$\hat{H}_{ED}(t)$, $\hat{H}_{EQ}(t)$, and $\hat{H}_{MD}(t)$ are the electric-dipole interaction, the electric-quadrupole interaction, and the magnetic-dipole interaction, respectively. The electric-dipole term is the dominating term in Eq. (6). Other contributions to $\hat{H}_I(t)$ are much smaller and, normally, need only to be considered for the weak transitions which are electric-dipole forbidden.

2.1. *Time-dependent approach, wave packets*

We let $|\Psi_M(t)\rangle$ denote the state vector of the isolated molecule at time t. The time evolution is given by:

$$i\hbar \frac{\partial |\Psi_M(t)\rangle}{\partial t} = \hat{H}_M |\Psi_M(t)\rangle \tag{7}$$

Time-evolution operators are defined by:

$$|\Psi_M(t)\rangle = \hat{U}_M(t, t_0)|\Psi_M(t_0)\rangle \tag{8}$$

and

$$|\Psi(t)\rangle = \hat{U}(t, t_0)|\Psi(t_0)\rangle \tag{9}$$

for the free molecule and the molecule in the radiation field, respectively. We insert these expressions into the time-dependent Schrödinger equations, Eqs. (7) and (4), and get the following equations for the time-evolution operators:

$$i\hbar \frac{\partial \hat{U}_M(t, t_0)}{\partial t} = \hat{H}_M \hat{U}_M(t, t_0) \tag{10}$$

and

$$i\hbar \frac{\partial \hat{U}(t, t_0)}{\partial t} = (\hat{H}_M + \hat{H}_I(t))\hat{U}(t, t_0) \tag{11}$$

Using these equations, we get:

$$\frac{d}{dt}\{\hat{U}_M^\dagger(t, t_0)\hat{U}(t, t_0)\} = -\frac{i}{\hbar}\hat{U}_M^\dagger(t, t_0)\hat{H}_I(t)\hat{U}(t, t_0) \tag{12}$$

and integration gives:

$$\hat{U}(t, t_0) = \hat{U}_M(t, t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt' \hat{U}_M(t, t')\hat{H}_I(t')\hat{U}(t', t_0) \tag{13}$$

Iteration gives:

$$\hat{U}(t, t_0) = \hat{U}_M(t, t_0) + \hat{U}^{(1)}(t, t_0) + \hat{U}^{(2)}(t, t_0) + \cdots \tag{14}$$

where

$$\begin{aligned}
\hat{U}_M(t, t_0) &= \exp(-i\hat{H}_M(t - t_0)/\hbar) \\
\hat{U}^{(1)}(t, t_0) &= -\frac{i}{\hbar}\int_{t_0}^{t} dt' \hat{U}_M(t, t')\hat{H}_I(t')\hat{U}_M(t', t_0) \qquad (15) \\
\hat{U}^{(2)}(t, t_0) &= -\frac{i}{\hbar}\int_{t_0}^{t} dt' \hat{U}_M(t, t')\hat{H}_I(t')\hat{U}^{(1)}(t', t_0)
\end{aligned}$$

In photofragmentation the initial state is a bound state of a molecule. Interaction with the radiation field creates a new state given by:

$$\begin{aligned}\hat{U}(t, t_0)\,|\Psi_M(t_0)\rangle &= \hat{U}_M(t, t_0)\,|\Psi_M(t_0)\rangle + \hat{U}^{(1)}(t, t_0)\,|\Psi_M(t_0)\rangle + \cdots \\ &= |\Psi_M(t)\rangle + |\Psi_M^{(1)}(t)\rangle + \cdots \qquad (16)\end{aligned}$$

To first order, probabilities of finding dissociative states can be extracted from the vector:

$$|\Psi_M^{(1)}(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\,\hat{U}_M(t, t')\hat{H}_I(t')\hat{U}_M(t', t_0)\,|\Psi_M(t_0)\rangle \qquad (17)$$

We consider now the explicit representation of Eq. (4) and the subsequent results concerning its solution for a *prototype molecule* with:

(a) 3 stationary electronic states,
(b) non-adiabatic coupling between electronic states 2 and 3, and
(c) radiative coupling between electronic states 1 and 2.

The state vector takes the form:

$$\langle \boldsymbol{q}, \boldsymbol{R}\,|\Psi(t)\rangle = \chi_1(\boldsymbol{R}, t)\psi_1(\boldsymbol{q}; \boldsymbol{R}) + \chi_2(\boldsymbol{R}, t)\psi_2(\boldsymbol{q}; \boldsymbol{R}) + \chi_3(\boldsymbol{R}, t)\psi_3(\boldsymbol{q}; \boldsymbol{R}) \qquad (18)$$

where $\boldsymbol{q}$ and $\boldsymbol{R}$ denote the electronic and nuclear coordinates, respectively. ψ_i ($i = 1, 2, 3$)) is an electronic eigenstate:

$$(\hat{T}_e + V(\boldsymbol{q}; \boldsymbol{R}))\psi_i(\boldsymbol{q}; \boldsymbol{R}) = E_i(\boldsymbol{R})\psi_i(\boldsymbol{q}; \boldsymbol{R}) \qquad (19)$$

The equation is solved for fixed values of $\boldsymbol{R}$, which plays the role of a parameter in the equation. This is indicated by ";" in the equation. The physical motivation for this form of the state vector is the fast motion of the electrons as compared to the slow motion of the nuclei. For bound state problems, fast motion is connected with large spacing between energy states. Thus, the energy spacing between the lowest electronic states is, normally, large and we need to consider only a few electronic states. Now we substitute this form of the state vector into Eq. (4) and obtain the following explicit representation for the *nuclear motion* in the presence of a radiation field:

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix}|\chi_1(t)\rangle \\ |\chi_2(t)\rangle \\ |\chi_3(t)\rangle\end{bmatrix} = \left(\begin{bmatrix}\hat{H}_1 & 0 & 0 \\ 0 & \hat{H}_2 & \hat{C}_{23} \\ 0 & \hat{C}_{32} & \hat{H}_3\end{bmatrix} + \begin{bmatrix}\hat{R}_{11}(t) & \hat{R}_{12}(t) & 0 \\ \hat{R}_{21}(t) & \hat{R}_{22}(t) & 0 \\ 0 & 0 & 0\end{bmatrix}\right)\begin{bmatrix}|\chi_1(t)\rangle \\ |\chi_2(t)\rangle \\ |\chi_3(t)\rangle\end{bmatrix} \qquad (20)$$

where

$$\begin{aligned}\hat{H}_i &= \hat{T}_n + E_i(\boldsymbol{R}) + \langle\psi_i|\hat{T}_n|\psi_i\rangle \\ \hat{C}_{ij} &= \langle\psi_i|\hat{T}_n|\psi_j\rangle - \sum_s \frac{\hbar^2}{2M_s}\langle\psi_i|\nabla_s|\psi_j\rangle\cdot\nabla_s \qquad (21) \\ \hat{R}_{ij}(t) &= \langle\psi_i|\hat{H}_{ED}(t)|\psi_j\rangle\end{aligned}$$

and integration in the matrix elements is over all electronic coordinates $\boldsymbol{q}$. Accordingly, the matrix elements are functions of the nuclear coordinates $\boldsymbol{R}$. Due to the orthonormality of the electronic eigenstates, the probability of finding the molecule in electronic "i" at time t given the nuclear position $\boldsymbol{R}$ is simply $|\chi_i(\boldsymbol{R}, t)|^2$.

We assume that electronic state 1 is a bound state of the molecule and that the molecule at time t_0 is in this state. In connection with the evaluation of Eq. (17), we note that:

$$\exp\left(-i\begin{bmatrix}\hat{H}_1 & 0 & 0\\ 0 & \hat{H}_2 & \hat{C}_{23}\\ 0 & \hat{C}_{32} & \hat{H}_3\end{bmatrix}(t'-t_0)/\hbar\right)\begin{bmatrix}|\chi_1(t_0)\rangle\\ 0\\ 0\end{bmatrix} = \begin{bmatrix}\exp(-i\hat{H}_1(t'-t_0)/\hbar)\,|\chi_1(t_0)\rangle\\ 0\\ 0\end{bmatrix} \tag{22}$$

since for the free molecule, the nuclear motion in electronic state 1 is decoupled from the other electronic states, and multiplication with the interaction matrix gives:

$$\begin{bmatrix}\hat{R}_{11}(t') & \hat{R}_{12}(t') & 0\\ \hat{R}_{21}(t') & \hat{R}_{22}(t') & 0\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix}\exp(-i\hat{H}_1(t'-t_0)/\hbar)\,|\chi_1(t_0)\rangle\\ 0\\ 0\end{bmatrix} = \begin{bmatrix}\hat{R}_{11}(t')\exp(-i\hat{H}_1(t'-t_0)/\hbar)\,|\chi_1(t_0)\rangle\\ \hat{R}_{21}(t')\exp(-i\hat{H}_1(t'-t_0)/\hbar)\,|\chi_1(t_0)\rangle\\ 0\end{bmatrix} \tag{23}$$

Thus, the physical interpretation of this equation is clear: The interaction with the radiation field at time t' transfers amplitude from electronic state 1 to state 2. We assume that unbound (dissociative) nuclear motion is possible in electronic state 2 and/or 3. The nuclear motion on surfaces 2 and 3, to first order in the interaction with the radiation field, is given by:

$$\begin{bmatrix}|\chi_2^{(1)}(t)\rangle\\ |\chi_3^{(1)}(t)\rangle\end{bmatrix} = -\frac{i}{\hbar}\int_{t_0}^{t} dt' \exp\left(-i\begin{bmatrix}\hat{H}_2 & \hat{C}_{23}\\ \hat{C}_{32} & \hat{H}_3\end{bmatrix}(t-t')/\hbar\right) \times \begin{bmatrix}\hat{R}_{21}(t')\exp(-i\hat{H}_1(t'-t_0)/\hbar)\,|\chi_1(t_0)\rangle\\ 0\end{bmatrix} \tag{24}$$

We choose $t_0 = 0$ and consider the situation where $|\chi_1\rangle$ is a vibrational-rotational eigenstate. We let ϵ_1 denote the associated energy. Furthermore, the electric field of the radiation field is plane polarized and represented such that:

$$\begin{aligned}\hat{R}_{21}(t') &= \langle\psi_2|-\vec{\mu}\cdot\vec{E}(t')|\psi_1\rangle\\ &= -\vec{\mu}_{21}\cdot\vec{E}_0 a(t')\cos\omega_l t'\end{aligned} \tag{25}$$

The unspecified form of the envelope function, $a(t')$, means that short pulse, long pulse laser fields, etc. are all under investigation. Thus, we get:

$$\begin{bmatrix}|\chi_2^{(1)}(t)\rangle\\ |\chi_3^{(1)}(t)\rangle\end{bmatrix} = \frac{i}{2\hbar}\int_0^t dt'\, e^{-i(\hbar\omega_l+\epsilon_1)t'/\hbar}a(t') \times \exp\left(-i\begin{bmatrix}\hat{H}_2 & \hat{C}_{23}\\ \hat{C}_{32} & \hat{H}_3\end{bmatrix}(t-t')/\hbar\right)|\phi(0)\rangle \tag{26}$$

where

$$|\phi(0)\rangle \equiv \begin{bmatrix} \vec{E}_0 \cdot \vec{\mu}_{21}|\chi_1(0)\rangle \\ 0 \end{bmatrix} \tag{27}$$

Two limiting forms are possible for the envelope function of the light pulse. One such limit is the *δ-function limit*, defined by:

$$a(t') = \delta(t' - t_p) \tag{28}$$

where $0 \leqslant t_p \leqslant t$. Thus, a light pulse is suddenly switched on and off at time $t = t_p$. From Eq. (26), we get:

$$\begin{bmatrix} |\chi_2^{(1)}(t)\rangle \\ |\chi_3^{(1)}(t)\rangle \end{bmatrix} = \frac{i}{2\hbar} \exp\left(-i \begin{bmatrix} \hat{H}_2 & \hat{C}_{23} \\ \hat{C}_{32} & \hat{H}_3 \end{bmatrix} (t - t_p)/\hbar \right) |\phi(0)\rangle \tag{29}$$

where an overall nonimportant phase factor, $\exp(-i(\hbar\omega_l + \epsilon_1)t_p/\hbar)$, has been neglected.

> *δ-function limit* for the light pulse:
> In this limit interaction with the radiation field, at time $t = t_p$, transfers suddenly amplitude from the ground to the excited state surface 2.
> Equation (29) shows that a wave packet, given as the product of the electronic transition dipole moment times the initial vibrational-rotational eigenstate of the molecule, is "vertically" excited.
> Subsequent to its creation this wave packet evolves on surface 2 and due to the non-adiabatic coupling terms, the wave packet evolution will ultimately produce wave packet amplitude on surface 3 as well.

The other limiting form for the light pulse is the *cw* (*continuous wave*) *limit*, defined by:

$$a(t') = 1 \tag{30}$$

and $t \to \infty$. Equation (26) takes now the form:

$$\begin{aligned} \begin{bmatrix} |\chi_2^{(1)}(t)\rangle \\ |\chi_3^{(1)}(t)\rangle \end{bmatrix} &= \frac{i}{2\hbar} \lim_{t\to\infty} e^{-iE_l t/\hbar} \int_0^t du\, e^{iE_l u/\hbar} \\ &\quad \times \exp\left(-i \begin{bmatrix} \hat{H}_2 & \hat{C}_{23} \\ \hat{C}_{32} & \hat{H}_3 \end{bmatrix} u/\hbar \right) |\phi(0)\rangle \end{aligned} \tag{31}$$

where $u = t - t'$ and $E_l = \hbar\omega_l + \epsilon_1$.

> *cw limit* for the light pulse:
> The interaction with the radiation field transfers continuously amplitude from the ground to the excited state 2.
> Equation (31) shows that wave packets, of the same form as in the δ-function limit, are "vertically" excited in the time interval from $u = 0$ to t.
> Subsequent to creation each wave packet evolve independently.
> The resulting nuclear state is obtained as a superposition of the wave packets.

Equations (29) and (31) are exact quantum mechanical descriptions of the Franck–Condon principle. In Sects. 3 and 4 where we calculate observables, we will show that these quantities can be expressed in terms of the wave packet describing the dynamics created in the δ-function limit (Eq. (29)).

Equation (31) is a half-Fourier transform of a time-dependent wave packet. We can characterize this state more when the non-adiabatic coupling terms can be neglected. In that case we have:

$$|\chi_2^{(1)}(t)\rangle = \frac{i}{2\hbar} \lim_{t\to\infty} e^{-iE_l t/\hbar}|\mathscr{R}\rangle \tag{32}$$

where [21]:

$$\begin{aligned}|\mathscr{R}\rangle &= \int_0^\infty du\, e^{iE_l u/\hbar} \exp(-i\hat{H}_2 u/\hbar)|\phi(0)\rangle \\ &= i\hbar\hat{G}(E_l^+)|\phi(0)\rangle\end{aligned} \tag{33}$$

and the Green's operator, $\hat{G}(E_l^+)$, is given by [20]:

$$\begin{aligned}\hat{G}(E_l^+) &= (E_l + i\epsilon - \hat{H}_2)^{-1} \\ &= -\frac{i}{\hbar}\int_0^\infty du\, e^{iE_l u/\hbar} \exp(-i\hat{H}_2 u/\hbar)\end{aligned} \tag{34}$$

where $\epsilon \to 0$. Thus, disregarding a phase factor the state $|\mathscr{R}\rangle$ is created in the cw limit. Using Eqs. (33) and (34):

$$(E_l - \hat{H}_2)|\mathscr{R}\rangle = i\hbar|\phi(0)\rangle \tag{35}$$

Assuming that $|\phi\rangle$ is real, the real and imaginary parts of this equation take the form:

$$\begin{aligned}\hat{H}_2|\mathscr{R}\rangle_r &= E_l|\mathscr{R}\rangle_r \\ \hat{H}_2|\mathscr{R}\rangle_i &= E_l|\mathscr{R}\rangle_i - \hbar|\phi(0)\rangle\end{aligned} \tag{36}$$

The real part, $|\mathscr{R}\rangle_r$, is accordingly an eigenstate of $\hat{H}_2$ at the energy E_l.

In the following sections where we calculate observables, we will show that these quantities in the *cw limit* can be expressed in terms of the real part of $|\mathscr{R}\rangle$.

2.2. *Time-independent approach, stationary scattering states*

It is instructive to have an alternative look at some of the results of the previous section in terms of stationary states (see, e.g., [22–24]). In order to keep the discussion as simple as possible, we neglect in the present section the non-adiabatic coupling terms. The dynamics is, accordingly, confined to the electronic state 2.

Equation (26) takes the form:

$$|\chi_2^{(1)}(t)\rangle = \frac{i}{2\hbar}\int_0^t dt'\, e^{-i(\hbar\omega_l + \epsilon_1)t'/\hbar} a(t') \exp(-i\hat{H}_2(t-t')/\hbar)|\phi(0)\rangle \tag{37}$$

The time evolution operator can be written in the form:

$$\exp(-i\hat{H}_2(t-t')/\hbar) = \sum_n \int dE\, |E, \boldsymbol{n}-\rangle\, e^{-iE(t-t')/\hbar} \langle E, \boldsymbol{n}-| \tag{38}$$

where:

$$\hat{H}_2|E, \boldsymbol{n}-\rangle = E|E, \boldsymbol{n}-\rangle \tag{39}$$

The stationary states can be discrete and continuous – the integration over energy in Eq. (38) is understood to be taken as a summation for the discrete part of the spectrum. $\boldsymbol{n}$ is a set of quantum numbers which labels the stationary states at energy E. The minus sign indicates that we have chosen one particular state in this subspace of degenerate states. The precise specification of these states is not needed – Eq. (39) suffices for the present discussion. We substitute Eq. (38) into Eq. (37):

$$|\chi_2^{(1)}(t)\rangle = \frac{i}{2\hbar}\sum_{\boldsymbol{n}}\int \langle E, \boldsymbol{n}-|\phi\rangle|E, \boldsymbol{n}-\rangle\, e^{-iEt/\hbar}\int_0^t dt'\, e^{-i(\hbar\omega_l+\epsilon_1-E)t'/\hbar}a(t')\, dE \tag{40}$$

This equation represents the nuclear wave packet expressed in terms of stationary states. The amplitude associated with the stationary state at energy E is given by the Franck–Condon factor $\langle E, \boldsymbol{n}-|\phi\rangle$. The overall energetic width of the state is given by the integral over t', which in turn depends on the envelope function of the light pulse.

Let us again analyse the results for the two limiting forms for this function. The *δ-function limit*, defined by Eq. (28):

$$|\chi_2^{(1)}(t)\rangle = \frac{i}{2\hbar}\sum_{\boldsymbol{n}}\int dE\langle E, \boldsymbol{n}-|\phi\rangle|E, \boldsymbol{n}-\rangle\, e^{-iE(t-t_p)/\hbar} \tag{41}$$

where an overall nonimportant phase factor, $\exp(-i(\hbar\omega_l+\epsilon_1)t_p/\hbar)$, has been neglected. Thus, the state $|\phi\rangle$ is resolved on the stationary states of the Hamiltonian $\hat{H}_2$.

The *cw-limit*, defined by Eq. (30):

$$|\chi_2^{(1)}(t)\rangle = \frac{i}{2\pi}\sum_{\boldsymbol{n}}\int dE\langle E, \boldsymbol{n}-|\phi\rangle|E, \boldsymbol{n}-\rangle\, e^{-iEt/\hbar}\int_0^\infty dt'\, e^{-i(\hbar\omega_l+\epsilon_1-E)t'/\hbar} \tag{42}$$

Now [18]:

$$\int_0^\infty dt'\, e^{-i(E_l-E)t'/\hbar} = \pi\hbar\delta(E-E_l) + i\hbar\mathscr{P}\int 1/(E_l-E) \tag{43}$$

where $E_l = \hbar\omega_l + \epsilon_1$ and $\mathscr{P}$ denotes a principal value integral. A comparison with Eq. (31) gives:

$$\begin{aligned}\int_0^\infty du\, e^{iE_l u/\hbar}\exp(-i\hat{H}_2 u/\hbar)|\phi\rangle &= \pi\hbar\sum_{\boldsymbol{n}}\langle E_l, \boldsymbol{n}-|\phi\rangle|E_l, \boldsymbol{n}-\rangle\\ &\quad + i\hbar\mathscr{P}\int\sum_{\boldsymbol{n}}\langle E, \boldsymbol{n}-|\phi\rangle|E, \boldsymbol{n}-\rangle\\ &\quad \times e^{i(E_l-E)t/\hbar}/(E_l-E)\, dE\end{aligned} \tag{44}$$

Now assuming that $|\phi\rangle$ is real, it is easy to show

$$\begin{aligned}Re\left\{\int_0^\infty du\, e^{iE_l u/\hbar}\exp(-i\hat{H}_2 u/\hbar)|\phi\rangle\right\} &= \tfrac{1}{2}\int_{-\infty}^\infty du\, e^{iE_l u/\hbar}\exp(-i\hat{H}_2 u/\hbar)|\phi\rangle\\ &= \pi\hbar\sum_{\boldsymbol{n}}\langle E_l, \boldsymbol{n}-|\phi\rangle|E_l, \boldsymbol{n}-\rangle \equiv |\mathscr{R}\rangle_r\end{aligned} \tag{45}$$

where Eq. (38) was used in the last line. The real part of $|\mathscr{R}\rangle$ is accordingly the projection of the initial state, $|\phi\rangle$, on the eigenstates of $\hat{H}_2$ at energy E_l.

3. The total reaction probability

The total absorption probability, at time t, is:

$$\begin{aligned} P_{tot}(\omega_l) &= \langle\chi_2^{(1)}(t)|\chi_2^{(1)}(t)\rangle + \langle\chi_3^{(1)}(t)|\chi_3^{(1)}(t)\rangle \\ &= \int |\chi_2^{(1)}(\boldsymbol{R}, t)|^2\, d\boldsymbol{R} + \int |\chi_3^{(1)}(\boldsymbol{R}, t)|^2\, d\boldsymbol{R} \end{aligned} \tag{46}$$

Using Eq. (26), we get:

$$\begin{aligned} P_{tot}(\omega_l) = \frac{1}{4\hbar^2} \int_0^t dt'' \int_0^t dt' a(t')a(t'')\, e^{iE_l(t''-t')/\hbar} \\ \times \langle\phi(0)|\hat{U}_M^\dagger(t, t'')\hat{U}_M(t, t')|\phi(0)\rangle \end{aligned} \tag{47}$$

where:

$$\hat{U}_M(t, t') = \exp\left(-i\begin{bmatrix} \hat{H}_2 & \hat{C}_{23} \\ \hat{C}_{32} & \hat{H}_3 \end{bmatrix}(t - t')/\hbar\right) \tag{48}$$

and integration in the matrix element is over the nuclear coordinates, $\boldsymbol{R}$. Now:

$$\begin{aligned} \hat{U}_M^\dagger(t, t'')\hat{U}_M(t, t') &= \hat{U}_M^{-1}(t, t'')\hat{U}_M(t, t') \\ &= \hat{U}_M(t'', t)\hat{U}_M(t, t') \\ &= \hat{U}_M(t'', t') \end{aligned} \tag{49}$$

We introduce new variables:

$$\begin{aligned} u &= t' - t'' \\ v &= t' + t'' \end{aligned} \tag{50}$$

and the volume element transforms as:

$$du\, dv = 2dt'\, dt'' \tag{51}$$

and we get:

$$\begin{aligned} P_{tot}(\omega_l) = \frac{1}{8\hbar^2} \int_0^{2t} dv \int_{-t}^t du a((v-u)/2)a((v+u)/2)\, e^{-iE_l u/\hbar} \\ \times \langle\phi(0)|\exp\left(i\begin{bmatrix} \hat{H}_2 & \hat{C}_{23} \\ \hat{C}_{32} & \hat{H}_3 \end{bmatrix} u/\hbar\right)|\phi(0)\rangle \end{aligned} \tag{52}$$

We consider now this result in the *cw limit* for the light pulse, defined by Eq. (30). We get:

$$P_{tot}(\omega_l) = \frac{t}{4\hbar^2} \int_{-t}^t du\, e^{iE_l u/\hbar}\langle\phi(0)|\hat{U}_M(u, 0)|\phi(0)\rangle \tag{53}$$

where $t \to \infty$.

It is instructive to consider an envelope function of the form:

$$a(t') = \left(\frac{8\gamma}{\pi}\right)^{1/4} e^{-\gamma t'^2} \tag{54}$$

which for $\gamma \to 0$ approach the cw limit. This function is normalized such that $\int_0^\infty |a(t')|^2\, dt' = 1$, i.e., it corresponds to a pulse with a fixed energy. Equation (52) takes now the form:

$$P_{tot}(\omega_l) = \frac{erf(\sqrt{2\gamma t})}{4\hbar^2} \int_{-t}^{t} du\, e^{-\gamma u^2/2}\, e^{iE_l u/\hbar} \langle \phi(0) | \hat{U}_M(u, 0) | \phi(0) \rangle \tag{55}$$

where *erf* is the error function, note that $erf(\infty) = 1$. For $t \to \infty$, we get:

$$P_{tot}(\omega_l) = \frac{1}{4\hbar^2} \int_{-\infty}^{\infty} \left(\frac{1}{2\pi\gamma} \right)^{1/2} e^{-E_l'^2/2\hbar^2\gamma}\, \widehat{au}(E_l - E_l')\, dE_l' \tag{56}$$

i.e., the convolution between the Fourier transforms of the light pulse and autocorrelation function:

$$\widehat{au}(E_l) = \int_{-\infty}^{\infty} du\, e^{iE_l u/\hbar} \langle \phi(0) | \hat{U}_M(u, 0) | \phi(0) \rangle \tag{57}$$

Note that for $\gamma \to 0$ we get the same result as in Eq. (53) (for the same pulse area).

It is easy to show that the right-hand sides in Eqs. (53) and (55) are real, as they should be. Thus, using:

$$\langle \phi(0) | \hat{U}_M(u, 0) | \phi(0) \rangle^* = \langle \phi(0) | \hat{U}_M^\dagger(u, 0) | \phi(0) \rangle = \langle \phi(0) | \hat{U}_M(-u, 0) | \phi(0) \rangle \tag{58}$$

we get:

$$\int_{-t}^{t} f(u)\, e^{iE_l u/\hbar} \langle \phi(0) | \hat{U}_M(u, 0) | \phi(0) \rangle\, du$$

$$= 2 \int_0^t Re\{ f(u)\, e^{iE_l u/\hbar} \langle \phi(0) | \hat{U}_M(u, 0) | \phi(0) \rangle \}\, du \tag{59}$$

where $f(u)$ is an even real-valued function. This equation shows, in addition, that a forward propagation in time, from $u = 0$ to $u = t$, is all that is needed.

Equations (55) and (56) make clear what we mean in terms of physics by the cw limit. γ should be so small that the function $\exp(-\gamma u^2/2)$ can be considered as constant on the time scale where the dynamics inherent in the autocorrelation function is important – or formulated in energy space – the width of the light pulse should be much smaller than the width of the features in the spectrum. When this condition is fulfilled, the envelope function in the integral of Eq. (55) can be replaced by unity and the total reaction probability is calculated as a Fourier transform of an autocorrelation function.

The dynamics inherent in the autocorrelation function is the dynamics of the molecule in the excited electronic states. For large u:

$$\hat{U}_M(u, 0) | \phi(0) \rangle = \hat{U}_M(u, 0) | \phi_d(0) \rangle + \hat{U}_M(u, 0) | \phi_b(0) \rangle \tag{60}$$

For simple dissociative motion $|\phi_d(0)\rangle$ will move away from the Franck–Condon region, i.e., the area vertically above the initial state, and never return. The autocorrelation function will decay to zero when $|\phi_d(0)\rangle$ is out of the Franck–Condon region. Actually, nodes in the wave packet associated with development of momentum will ensure that the decay to zero happens before the wave packet is out of the Franck–Condon region. It takes typically much less than a vibrational period for the molecule. The exact details depends of course on the steepness of the potential, the reduced mass of the separating fragments, etc. For more complicated dissociative motion parts of $|\phi_d(0)\rangle$ can revisit the Franck–Condon region a few times. The autocorrelation function will decay to zero within the order of a vibrational period for the molecule. For bound motion $|\phi_b(0)\rangle$ will revisit the Franck–Condon region several times. Many recurrences in the autocorrelation function will, accordingly, show up. However, a spectrum with "experimental" resolution can still be obtained by considering only a limited number of these recurrences [4].

> Definition of *cw limit* for the total absorption spectrum:
> The envelope function of the light pulse should be constant until the dynamics in the autocorrelation function is determined.
> For dissociation this happens typically within a vibrational period.
> For bound motion it takes a few vibrational periods.
> Fast decay of the autocorrelation function implies that the cw limit for the light pulse is reached even for a quite short pulse.

This limit defines the situation where the highest possible resolution in energy is obtained. In practice, almost all situations fall within this limit. We calculate the total probability from:

$$P_{tot}(\omega_l) = \frac{1}{2\hbar^2}\int_0^\infty Re\left\{e^{iE_l u/\hbar}\langle\phi(0)|\exp\left(-i\begin{bmatrix}\hat{H}_2 & \hat{C}_{23}\\ \hat{C}_{32} & \hat{H}_3\end{bmatrix}u/\hbar\right)|\phi(0)\rangle\right\}du \tag{61}$$

We observe:

> **The total absorption probability in the *cw limit* is expressed in terms of the real-time dynamics of the molecule as created in the *δ-function limit*. The dynamics is mapped out in the Franck–Condon region due to the overlap with the initial state.**
> **Measurement in the energy (frequency) – domain of the total absorption spectrum is accordingly a way to get information about dynamics in the Franck–Condon region.**

If we do the half-Fourier transform of the time evolved $|\phi(0)\rangle$ before taking the overlap with the initial state, we can – in the limit of no non-adiabatic coupling – also express Eq. (61) in the form (compare Eq. (33)):

$$P_{tot}(\omega_l) = \frac{1}{2\hbar^2}\langle\phi(0)|\mathscr{R}\rangle_r \tag{62}$$

i.e., an overlap between the initial state and the real part of $|\mathscr{R}\rangle$ – the stationary state created in the *cw limit*. A more conventional expression in terms of a set of stationary states is obtained if we use Eq. (45):

$$P_{tot}(\omega_l) = \frac{\pi}{2\hbar}\sum_n |\langle\phi(0)|E_l, \mathbf{n}-\rangle|^2 \tag{63}$$

Note, however, that in the two last expressions for the absorption probability *the explicit reference to molecular dynamics is lost.*

4. Final product distributions

So far we have not explored the fact that the molecule might dissociate and free fragments can show up when it is excited electronically. The formulas derived in the previous sections are, in fact, also valid in situations where the molecule does not dissociate at all. In the preceding section we calculated the total probability associated with the transition from the left- to the right-hand side in the equation:

$$ABC(n) + \hbar\omega_l \rightarrow \begin{cases} ABC \\ A + BC \\ B + AC \\ C + AB \\ A + B + C \end{cases} \tag{64}$$

Now we want to calculate the probability associated with the channels which corresponds to bond breaking and focus on the chemical composition of the fragments as well as more detailed questions concerning the exact quantum state of the fragments.

4.1. *Detailed final product distribution*

The state of the fragments in arrangement channel α, is given by:

$$\hat{H}_i^\alpha |E, i, n_\alpha\rangle = E|E, i, n_\alpha\rangle \tag{65}$$

where $\hat{H}_i^\alpha$ is the nuclear Hamiltonian of arrangement channel α [20] and electronic state i ($=2$ or 3). n_α is a collective symbol for the vibrational and rotational quantum numbers and the momentum vector associated with the relative motion of the fragments. Using Eq. (26), we get the following expression for the probability of finding fragments in these states:

$$\begin{bmatrix} |\langle E, 2, n_\alpha|\chi_2^{(1)}(t)\rangle|^2 \\ |\langle E, 3, n_\alpha|\chi_3^{(1)}(t)\rangle|^2 \end{bmatrix} = \frac{1}{4\hbar^2}\left|\int_0^t dt'\, e^{-iE_l t'/\hbar} a(t') \begin{bmatrix} \langle E, 2, n_\alpha| \\ \langle E, 3, n_\alpha| \end{bmatrix}\right.$$
$$\left. \times \exp\left(-i\begin{bmatrix} \hat{H}_2 & \hat{C}_{23} \\ \hat{C}_{32} & \hat{H}_3 \end{bmatrix}(t-t')/\hbar\right)\begin{bmatrix} |\phi_d(0)\rangle \\ 0 \end{bmatrix}\right|^2 \tag{66}$$

In order to simplify, let us neglect the non-adiabatic coupling terms and focus on the nuclear dynamics associated with electronic state 2. Dissociation implies [20]:

$$\lim_{t\rightarrow\infty} \exp(-i\hat{H}_2 t/\hbar)|\phi_d(0)\rangle = \sum_\alpha \exp(-i\hat{H}_2^\alpha t/\hbar)|\psi_{out}^\alpha\rangle \tag{67}$$

Thus:

$$|\psi_{out}^\alpha\rangle = \hat{\Omega}_-^{\alpha\dagger}|\phi_d(0)\rangle \tag{68}$$

where:

$$\hat{\Omega}_-^\alpha = \lim_{t\rightarrow\infty} \exp(i\hat{H}_2 t/\hbar)\exp(-i\hat{H}_2^\alpha t/\hbar) \tag{69}$$

is the channel Møller operator for channel α [20]. Equation (67) expresses the fact that after dissociation ($t \rightarrow \infty$) freely moving fragments can show up in the different arrangement channels.

We assume that the light pulse interacts with the molecule in a finite, but possibly very long, time t_l. Thus, $a(t') = 0$ for $t' > t_l$. The product distribution is then calculated for $t \to \infty$, which in practice means that $t - t_l > t_{diss}$, i.e., $t > t_{diss} + t_l$. Using Eqs. (65) and (67) we get:

$$\lim_{t \to \infty} |\langle E, 2, n_\alpha | \chi_2^{(1)}(t) \rangle|^2 = \frac{1}{4\hbar^2} \left| \int_0^{t_l} dt'\, e^{-i(E_l - E)t'/\hbar} a(t') \right|^2 \sum_{\alpha'} |\langle E, 2, n_\alpha | \psi_{out}^{\alpha'} \rangle|^2 \tag{70}$$

where the second factor is a constant and Eqs. (68) and (69) give:

$$\sum_{\alpha'} |\langle E, 2, n_\alpha | \psi_{out}^{\alpha'} \rangle|^2 = \lim_{t \to \infty} |\langle E, 2, n_\alpha | \exp(-i\hat{H}_2 t/\hbar) | \phi_d(0) \rangle|^2 \tag{71}$$

Thus, *the probability of finding a product in the state* $|E, 2, n_\alpha\rangle$ is:

$$P(E, 2, n_\alpha) = \frac{|\epsilon(\omega)|^2}{4\hbar^2} \lim_{t \to \infty} |\langle E, 2, n_\alpha | \exp(-i\hat{H}_2 t/\hbar) | \phi_d(0) \rangle|^2 \tag{72}$$

where:

$$\epsilon(\omega) = \int_0^{t_l} dt'\, e^{-i\omega t'} a(t') \tag{73}$$

and $\omega = (E_l - E)/\hbar$.

This result can be considered for different forms of the light pulse.

In the *δ-function limit*:

$$|\epsilon(\omega)|^2 = |e^{-i\omega t_p}|^2 = 1 \tag{74}$$

Thus, product states with various energies can be formed. The energies are determined by the energetic width of the asymptotic form of the wave packet. In practice, this limit is obtained when the energetic width of the light pulse is much larger than the energetic width of the wave packet. In time space this implies, $t_l \ll t_{diss}$.

In the *cw limit*:

$$|\epsilon(\omega)|^2 = \left| \int_0^{t_l} dt'\, e^{-i\omega t'} \right|^2 = 4 \sin^2(\omega t_l/2)/\omega^2 \tag{75}$$

and

$$\lim_{t_l \to \infty} |\epsilon(\omega)|^2/t_l = \lim_{t_l \to \infty} 4 \sin^2(\omega t_l/2)/(\omega^2 t_l) = 2\pi\delta(\omega) = 2\pi\hbar\delta(E_l - E) \tag{76}$$

Thus, for sufficiently long times, the accessible product states have an energy which is determined by the energy of the photon. In practice, this limit is obtained when $t_l \gg t_{diss}$.

An intermediate case given by the Gaussian pulse shape defined in Eq. (54) gives:

$$|\epsilon(\omega)|^2 = \left| \left(\frac{8\gamma}{\pi}\right)^{1/4} \int_0^{t_l} dt'\, e^{-i\omega t'} e^{-\gamma t'^2} \right|^2 = erf(\sqrt{2\gamma} t_l) \int_{-t_l}^{t_l} e^{-\gamma u^2/2} e^{i\omega u}\, du \tag{77}$$

For some given γ and t_l large, we get:

$$\lim_{t_l \to \infty} |\epsilon(\omega)|^2 = \int_{-\infty}^{\infty} e^{-\gamma u^2/2} e^{i\omega u}\, du = 2\pi \left(\frac{1}{2\pi\gamma}\right)^{1/2} e^{-\omega^2/2\gamma} \tag{78}$$

which for small γ approach $2\pi\delta(\omega)$, i.e., the cw limit. We observe from Eq. (72):

The detailed final product distribution is expressed in terms of the real-time dynamics of the molecule as created in the δ-function limit.
The dynamics is mapped out in the product region.
Measurement of the final product distribution is accordingly a way to get information about the dynamics all the way from the Franck–Condon region to the product region.

The results of this section show in addition that the product distribution is affected by the form of the light pulse. A form of control of the outcome of the reaction can accordingly be performed in this way. However, the product distribution obtained with a δ-function pulse can also be obtained in the cw limit if the frequency of the light is varied. In addition, it is clear that at a given energy, the form of the light pulse will not affect the *relative* probabilities of obtaining the different (degenerate) channels. Real control of the outcome requires, at least, two laser pulses! [25].

4.2. Branching between chemically distinct products

The most detailed information obtainable from photodissociation dynamics is the state-to-state probabilities calculated in the previous section. However, often less detailed information suffices. This can, of course, be obtained by appropriate summation over the detailed state-to-state information – but a more direct calculational approach can be available – as illustrated in the present section for the branching between chemically distinct products. Thus, we calculate here the probability of forming given chemical products irrespective of the particular quantum state of the product [10].

Assume now that two different arrangement channels are open, e.g.:

$$ABC(n) + \hbar\omega_l \rightarrow \begin{cases} A + BC(n_1) \\ C + AB(n_2) \end{cases} \tag{79}$$

For the wave packet dynamics inherent in Eq. (72), this situation implies according to Eq. (67):

$$\lim_{t\rightarrow\infty} \exp(-i\hat{H}_2 t/\hbar)\,|\phi_d(0)\rangle = \exp(-i\hat{H}_2^1 t/\hbar)\,|\psi^1_{out}\rangle + \exp(-i\hat{H}_2^2 t/\hbar)\,|\psi^2_{out}\rangle \tag{80}$$

where $|\psi^1_{out}\rangle$ and $|\psi^2_{out}\rangle$ denote the asymptotic form of the state vector in channels 1 and 2, respectively. Now the probability of finding the system in, say, arrangement channel 1 in the eigenstate $|E, 2, n_1\rangle$ is (Eq. (72)):

$$\begin{aligned} P(E, 2, n_1) &= \mathscr{C} \lim_{t\rightarrow\infty} |\langle E, 2, n_1|\exp(-i\hat{H}_2 t/\hbar)\,|\phi_d(0)\rangle|^2 \\ &= \mathscr{C}\,|\langle E, 2, n_1|\psi^1_{out}(t)\rangle|^2 + \mathscr{C}\,|\langle E, 2, n_1|\psi^2_{out}(t)\rangle|^2 \\ &\quad + \mathscr{C}\langle\psi^1_{out}(t)|E, 2, n_1\rangle\langle E, 2, n_1|\psi^2_{out}(t)\rangle \\ &\quad + \mathscr{C}\langle\psi^2_{out}(t)|E, 2, n_1\rangle\langle E, 2, n_1|\psi^1_{out}(t)\rangle \end{aligned} \tag{81}$$

where

$$|\psi^1_{out}(t)\rangle = \exp(-i\hat{H}_2^1 t/\hbar)\,|\psi^1_{out}\rangle \tag{82}$$

and

$$|\psi^2_{out}(t)\rangle = \exp(-i\hat{H}_2^2 t/\hbar)\,|\psi^2_{out}\rangle \tag{83}$$

and $\mathscr{C}$ denotes $|\epsilon(\omega)|^2/4\hbar^2$. The assumption of no overlap between the eigenstates of the two arrangement channels is now introduced, i.e.:

$$\langle E, 2, n_1 | E, 2, n_2 \rangle = 0 \tag{84}$$

this implies that $\langle E, 2, n_1 | \psi^2_{out}(t) \rangle = 0$. Thus, the last three terms of Eq. (81) all disappear under this assumption. Another way to state the implications of Eq. (84) is that interference terms between $|\psi^1_{out}(t)\rangle$ and $|\psi^2_{out}(t)\rangle$ disappear in the probability amplitude associated with the total wave function.

The probability of finding the system in arrangement channel 1 irrespective of the particular quantum state n_1 and integrated over the total energy E, gives the absorption probability into arrangement channel 1 as a function of the photon frequency. Using a well-known derivation [26], we get in the *cw limit* for the electromagnetic radiation ($E_l = \hbar\omega_l + \epsilon_1$):

$$\begin{aligned}
P_1(\omega_l) &= \frac{\pi}{2\hbar}\int \sum_{n_1} |\langle E, 2, n_1 | \exp(-i\hat{H}^1_2 t/\hbar) | \psi^1_{out}\rangle|^2 \delta(E - E_l)\, dE \\
&= \frac{\pi}{2\hbar}\int \sum_{n_1} |\langle E, 2, n_1 | \psi^1_{out}\rangle|^2 \delta(E - E_l)\, dE \\
&= \frac{1}{4\hbar^2}\int \sum_{n_1} \int_{-\infty}^{\infty} d\tau\, e^{i(E_l - E)\tau/\hbar} |\langle E, 2, n_1 | \psi^1_{out}\rangle|^2\, dE \\
&= \frac{1}{4\hbar^2}\int \sum_{n_1} \int_{-\infty}^{\infty} d\tau\, e^{iE_l\tau/\hbar} \langle \psi^1_{out} | \exp(-i\hat{H}^1_2 \tau/\hbar) | E, 2, n_1\rangle\langle n_1, 2, E | \psi^1_{out}\rangle\, dE \\
&= \frac{1}{4\hbar^2}\int_{-\infty}^{\infty} e^{iE_l\tau/\hbar} \langle \psi^1_{out} | \exp(-i\hat{H}^1_2 \tau/\hbar) | \psi^1_{out}\rangle\, d\tau
\end{aligned} \tag{85}$$

where the completeness of the eigenstates of $\hat{H}^1_2$ was used, i.e.:

$$\int \sum_{n_1} |E, 2, n_1\rangle\langle n_1, 2, E|\, dE = \hat{I} \tag{86}$$

Note, in actual calculations what is known is not $|\psi^1_{out}\rangle$ but (compare Eq. (80)):

$$|\psi^1_{out}(t_f)\rangle = \exp(-i\hat{H}^1_2 t_f/\hbar)|\psi^1_{out}\rangle \tag{87}$$

where t_f is the final propagation time. However:

$$\begin{aligned}
P_1(\omega_l) &= \frac{1}{4\hbar^2}\int_{-\infty}^{\infty} d\tau\, e^{iE_l\tau/\hbar} \langle \psi^1_{out} | \exp(-i\hat{H}^1_2 \tau/\hbar) | \psi^1_{out}\rangle \\
&= \frac{1}{4\hbar^2}\int_{-\infty}^{\infty} d\tau\, e^{iE_l\tau/\hbar} \langle \psi^1_{out}(t_f) | \psi^1_{out}(t_f + \tau)\rangle \\
&= \frac{1}{2\hbar^2}\int_{0}^{\infty} d\tau\, Re\{e^{iE_l\tau/\hbar} \langle \psi^1_{out}(t_f) | \psi^1_{out}(t_f + \tau)\rangle\}
\end{aligned} \tag{88}$$

A completely equivalent formula can, of course, be derived for products in arrangement channel 2:

$$P_2(\omega_l) = \frac{1}{2\hbar^2}\int_{0}^{\infty} d\tau\, Re\{e^{iE_l\tau/\hbar} \langle \psi^2_{out}(t_f) | \psi^2_{out}(t_f + \tau)\rangle\} \tag{89}$$

The ratio $P_1(\omega_l)/P_2(\omega_l)$ gives the branching ratio between the two chemically distinct products as a function of the photon frequency ω_l. The two wave packets $|\psi^1_{out}(t_f)\rangle$ and $|\psi^2_{out}(t_f)\rangle$ are according to Eq. (80) given as the part of the initial state evolving into channels 1 and 2, respectively. They are easily identified in pratice [11, 12]. The correlation functions for these wave packets will decay to zero very fast due to the translational motion of the fragments.

The interpretation of the form of Eqs. (88) and (89) is simple. The Fourier transform of the autocorrelation function gives the energy spectrum of the state. For each of the states, $|\psi^1_{out}(t_f)\rangle$ and $|\psi^2_{out}(t_f)\rangle$, Eqs. (88) and (89), respectively, gives the probability of finding the component of the state at energy $E_l = \hbar\omega_l + \epsilon_1$. Thus, the branching ratio, at energy $E_l = \hbar\omega_l + \epsilon_1$, is the ratio between the probabilities of finding the component of the states $|\psi^1_{out}(t_f)\rangle$ and $|\psi^2_{out}(t_f)\rangle$ at this energy.

5. Semi-classical description via the Wigner phase space representation

Our intuition about dynamics is strongly connected to classical mechanics. In order to get a better feel for the results of Sects. 3 and 4, we now turn to a description using classical mechanics for the time evolution.

A convenient way to make contact with classical mechanics is to use the Wigner phase space representation of quantum mechanics [27–29]. This is an exact representation of quantum mechanics which has the appealing feature of containing many elements which appear to be very close to a classical description. Thus, operators are represented by functions on phase space and quantum mechanical states are represented by the so-called Wigner function [27]. This is a function defined on phase space which makes the proper transition from the classical description of the state, given by a single point in phase space, to the quantum mechanical description where uncertainty relations, etc. have to be obeyed.

The phase space equivalent of the expectation value of an operator is:

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \int\int a(\boldsymbol{p}, \boldsymbol{q})\Gamma(\boldsymbol{p}, \boldsymbol{q}, t)\, d\boldsymbol{p}\, d\boldsymbol{q} \tag{90}$$

where $a(\boldsymbol{p}, \boldsymbol{q})$ is the classical function corresponding to the operator $\hat{A}$. $a(\boldsymbol{p}, \boldsymbol{q})$ is defined by:

$$a(\boldsymbol{p}, \boldsymbol{q}) = (2)^N \int d\boldsymbol{\eta}\langle\boldsymbol{q} - \boldsymbol{\eta}|\hat{A}|\boldsymbol{q} + \boldsymbol{\eta}\rangle \exp(2i\boldsymbol{p}\cdot\boldsymbol{\eta}/\hbar) \tag{91}$$

and $\Gamma(\boldsymbol{p}, \boldsymbol{q}, t)$ is the Wigner function defined by:

$$\begin{aligned}\Gamma(\boldsymbol{p}, \boldsymbol{q}, t) &= \left(\frac{1}{\pi\hbar}\right)^N \int d\boldsymbol{\eta}\langle\boldsymbol{q} - \boldsymbol{\eta}|\psi(t)\rangle\langle\psi(t)|\boldsymbol{q} + \boldsymbol{\eta}\rangle \exp(2i\boldsymbol{p}\cdot\boldsymbol{\eta}/\hbar)\\ &= \left(\frac{1}{\pi\hbar}\right)^N \int d\boldsymbol{\eta}\psi(\boldsymbol{q} + \boldsymbol{\eta}, t)^*\psi(\boldsymbol{q} - \boldsymbol{\eta}, t) \exp(2i\boldsymbol{p}\cdot\boldsymbol{\eta}/\hbar)\end{aligned} \tag{92}$$

where $\psi(\boldsymbol{q}, t) = \langle\boldsymbol{q}|\psi(t)\rangle$ and N is number of degrees of freedom. A comparison of Eqs. (91) and (92) shows that the Wigner function is the phase space function associated with the projection operator, $(2\pi\hbar)^{-N}|\psi(t)\rangle\langle\psi(t)|$.

The time evolution of the Wigner function is given by:

$$\Gamma(\boldsymbol{p}, \boldsymbol{q}, t) = \exp(-i\hat{L}t/\hbar)\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0) \tag{93}$$

where $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$ is the Wigner function at time zero and $\exp(-i\hat{L}t/\hbar)$ is the phase space counterpart to the time evolution operator. $\hat{L}$ is the quantum Liouville operator:

$$\hat{L} = 2i \sin\left[\frac{\hbar}{2}\left(\frac{\partial H}{\partial \boldsymbol{q}} \cdot \frac{\partial}{\partial \boldsymbol{p}} - \frac{\partial H}{\partial \boldsymbol{p}} \cdot \frac{\partial}{\partial \boldsymbol{q}}\right)\right] \tag{94}$$

where H is the *classical* Hamiltonian corresponding to $\hat{H}$. $\hat{L}$ is a complicated operator containing derivatives in $\boldsymbol{p}$ and $\boldsymbol{q}$ of infinite-order. However, the power of this equation lies in its potential for making contact with classical mechanics. If we at each phase space point neglect all anharmonic terms in the potential (i.e., a local harmonic approximation), the quantum Liouville operator reduces to the classical Liouville operator and each phase space point evolves according to classical mechanics. This approximation has been studied in some detail in the literature [30, 31]. Its validity is limited to short times and situations where anharmonicities are unimportant.

Now, let us consider the form of Eqs. (61), (72), and (88) in the phase space representation.

5.1. Total absorption probability

Using Eqs. (61) and (38) or (63) and Eq. (90) in order to get the phase space equivalent of a projection operator, we find [32]:

$$\begin{aligned} P_{tot}(\omega_l) &= \frac{1}{4\hbar^2}\langle\phi(0)|\int_{-\infty}^{\infty} \exp\{i(E_l - \hat{H}_2)u/\hbar\}\, du\,|\phi(0)\rangle \\ &= \frac{\pi}{2\hbar}\sum_{\boldsymbol{n}}^{open} \langle\phi(0)|E_l, \boldsymbol{n}-\rangle\langle E_l, \boldsymbol{n}-|\phi(0)\rangle \\ &= \frac{\pi}{2\hbar}(2\pi\hbar)^N \int\int \sum_{\boldsymbol{n}}^{open} \Gamma_{\boldsymbol{n}}^{E_l}(\boldsymbol{p}, \boldsymbol{q})\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)\, d\boldsymbol{p}\, d\boldsymbol{q} \end{aligned} \tag{95}$$

where $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$ is the Wigner function associated with $|\phi(0)\rangle$ and $\Gamma_{\boldsymbol{n}}^{E_l}(\boldsymbol{p}, \boldsymbol{q})$ is the Wigner function associated with the state $|E_l, \boldsymbol{n}-\rangle$.

We can consider approximations to the sum over Wigner functions or, equivalently, approximations to the phase space equivalent of the operator $\int_{-\infty}^{\infty} \exp\{i(E_l - \hat{H}_2)u/\hbar\}\, du$. The approximations derived in [32] are especially well suited for fast dissociation processes:

$$(2\pi\hbar)^N \sum_{\boldsymbol{n}}^{open} \Gamma_{\boldsymbol{n}}^{E_l}(\boldsymbol{p}, \boldsymbol{q}) = \delta(H_2(\boldsymbol{p}, \boldsymbol{q}) - E_l) + \cdots \tag{96}$$

Thus, Eq. (95) takes the form:

$$P_{tot}(\omega_l) = \frac{\pi}{2\hbar}\int\int \delta(H_2(\boldsymbol{p}, \boldsymbol{q}) - E_l)\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)\, d\boldsymbol{p}\, d\boldsymbol{q} \tag{97}$$

The delta function selects those points in phase space which have a classical energy equal to $E_l = \hbar\omega_l + \epsilon_1$. The probability becomes accordingly the sum (integral) of weights (given by $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$) for these phase space points.

5.2. Branching between chemically distinct products

In order to write down the phase space equivalent of Eq. (88), we proceed in the same way as for the total absorption [10]. We get a simple exact phase space expression for the partial probability $P_1(\omega_l)$, if we make explicit reference to the eigenstates of $\hat{H}_2^1$. Thus, we use:

$$\exp(-i\hat{H}_2^1\tau/\hbar) = \int \sum_{n_1} |E, 2, n_1\rangle\langle n_1, 2, E|\, e^{-iE\tau/\hbar}\, dE \qquad (98)$$

and Eq. (88) takes the form:

$$\begin{aligned} P_1(\omega_l) &= \frac{1}{4\hbar^2}\langle\psi^1_{out}(t_f)|\int_{-\infty}^{\infty} \exp\{i(E_l - \hat{H}_2^1)\tau/\hbar\}\, d\tau\, |\psi^1_{out}(t_f)\rangle \\ &= \frac{\pi}{2\hbar}\sum_{n_1}^{open} \langle\psi^1_{out}(t_f)|E_l, 2, n_1\rangle\langle n_1, 2, E_l|\psi^1_{out}(t_f)\rangle \\ &= \frac{\pi}{2\hbar}(2\pi\hbar)^N \int\!\!\int \sum_{n_1}^{open} \Gamma^{E_l}_{n_1}(\boldsymbol{p}, \boldsymbol{q})\Gamma^1_{out}(\boldsymbol{p}, \boldsymbol{q}, t_f)\, d\boldsymbol{p}\, d\boldsymbol{q} \end{aligned} \qquad (99)$$

where $\Gamma^1_{out}(t_f)$ is the Wigner function associated with $|\psi^1_{out}(t_f)\rangle$ and $\Gamma^{E_l}_{n_1}$ is the Wigner function associated with the state $|E_l, 2, n_1\rangle$. The summation runs over all open (degenerate) states at energy E_l.

We can now make contact with classical mechanics. First, classical mechanics for the time evolution gives:

$$\Gamma^1_{out}(\boldsymbol{p}, \boldsymbol{q}, t_f) = \{\exp(-i\hat{L}_Q t_f/\hbar)\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)\}_1 \qquad (100)$$

where $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$ denotes the Wigner function associated with $|\phi(0)\rangle$, $\hat{L}_Q$ is the classical Liouville operator given by the first term in the expansion of the sin[ ] function of Eq. (94), and $\{\ \}_1$ indicates that we look at the trajectories which show up in channel 1. Thus, Eq. (99) with the approximation of Eq. (100), tell us that in order to find the probability of having a product in channel 1 at the energy $E_l = \hbar\omega_l + \epsilon_1$, we have to run a swarm of trajectories with weights chosen according to the initial Wigner function $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$. Trajectories which end up in channel 1 are subsequently weighted by the function $\sum_{n_1} \Gamma^{E_l}_{n_1}$, and the result is obtained as a sum (integral) over all such weights associated with trajectories in the swarm. This summation will contain trajectories "off the energy shell", i.e., trajectories with energies different from E_l.

Second, we can consider approximations to the sum over final state Wigner functions or, equivalently, approximations to the phase space equivalent of the operator $\int_{-\infty}^{\infty} \exp\{i(E_l - \hat{H}_2^1)\tau/\hbar\}\, d\tau$. We use the same analysis which gave Eq. (96), this is completely applicable in the present situation when the free translational motion of the fragments is fast:

$$(2\pi\hbar)^N \sum_{n_1}^{open} \Gamma^{E_l}_{n_1}(\boldsymbol{p}, \boldsymbol{q}) = \delta(H_2^1(\boldsymbol{p}, \boldsymbol{q}) - E_l) + \cdots \qquad (101)$$

Note that there is no reference to the quantum number n_1 on the right-hand side of this equation. Thus, using the approximations in Eqs. (100) and (101), Eq. (99) takes the form:

$$P_1(\omega_l) = \frac{\pi}{2\hbar}\int\!\!\int \delta(H_2^1(\boldsymbol{p}, \boldsymbol{q}) - E_l)\{\exp(-i\hat{L}_Q t_f/\hbar)\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)\}_1\, d\boldsymbol{p}\, d\boldsymbol{q} \qquad (102)$$

The delta function selects those trajectories in channel 1 which have the specified energy (E_l). The probability becomes accordingly the sum (integral) of weights (given by $\Gamma(\boldsymbol{p}, \boldsymbol{q}, 0)$) for these trajectories. Using that energy is conserved for a classical trajectory, this probability can also be calculated as the sum of weights for trajectories which at $t = 0$ have the energy E_l and which sooner or later will move into channel 1. Thus, with the approximations introduced above the equation for the probability of having a fragment in channel 1 at energy E_l, takes a simple and intuitive form. The derivations leading to Eq. (102) have shown the nature of approximations involved in this equation. Therefore, it is possible to estimate the validity of this expression and correction terms can be included systematically, e.g., by considering higher order terms in Eq. (101) as discussed in [32].

5.3. Detailed final product distribution

Equation (72) takes the form:

$$\begin{aligned} P(E, 2, n_\alpha) &= \frac{|\epsilon(\omega)|^2}{4\hbar^2} \lim_{t \to \infty} |\langle E, 2, n_\alpha | \exp(-i\hat{H}_2 t/\hbar) | \phi(0) \rangle|^2 \\ &= \frac{|\epsilon(\omega)|^2}{4\hbar^2} \langle \psi_{out}(t_f) | E, 2, n_\alpha \rangle \langle E, 2, n_\alpha | \psi_{out}(t_f) \rangle \\ &= \frac{|\epsilon(\omega)|^2}{4\hbar^2} (2\pi\hbar)^N \int\!\!\int \Gamma^E_{n_\alpha}(\boldsymbol{p}, \boldsymbol{q}) \Gamma_{out}(\boldsymbol{p}, \boldsymbol{q}, t_f) \, d\boldsymbol{p} \, d\boldsymbol{q} \end{aligned} \tag{103}$$

where $\Gamma_{out}(\boldsymbol{p}, \boldsymbol{q}, t_f)$ is the Wigner function associated with the state:

$$|\psi_{out}(t_f)\rangle = \exp(-i\hat{H}_2 t_f/\hbar) | \phi(0) \rangle \tag{104}$$

and t_f is the final propagation time.

We can now introduce approximations. Classical mechanics for the time evolution:

$$\Gamma_{out}(\boldsymbol{p}, \boldsymbol{q}, t_f) = \exp(-i\hat{L}_Q t_f/\hbar) \Gamma(\boldsymbol{p}, \boldsymbol{q}, 0) \tag{105}$$

etc.

Finally, the origin of the vertical transition idea for positions and momenta (classical Franck–Condon principle), used in classical formulations [33, 34] should be clear from the discussion above. It is already present in the phase space equations before classical approximations are introduced, accordingly it is a consequence of the basic approximations – the adiabatic approximation and the use of first order perturbation theory for the light-matter interaction.

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References

1. Kulander KC, Heller EJ (1978) J Chem Phys 69:2439
2. Lee Soo-Y, Heller EJ (1979) J Chem Phys 71:4777
3. Lee Soo-Y, Heller EJ (1982) J Chem Phys 76:3035
4. Heller EJ (1981) Acc Chem Res 14:368

5. Rama Krishna MV, Coalson RD (1988) Chem Phys 120:327
6. Coalson RD (1987) J Chem Phys 86:6823
7. Jiang Xue-P, Heather R, Metiu H (1989) J Chem Phys 90:2555
8. Engel V, Schinke R, Hennig S, Metiu H (1990) J Chem Phys 92:1
9. Engel V, Metiu H (1990) J Chem Phys 92:2317
10. Henriksen NE (1990) Chem Phys Letters 169:229
11. Henriksen NE, Zhang J, Imre DG (1988) J Chem Phys 89:5607
12. Zhang J, Imre DG, Frederick JH (1989) J Phys Chem 93:1840
13. Henriksen NE, Heller EJ (1989) J Chem Phys 91:4700
14. Heller EJ, Stechel EB, Davis MJ (1980) J Chem Phys 73:4720
15. Williams SO, Imre DG (1988) J Phys Chem 92:3374
16. Dantos M, Rosker MJ, Zewail AH (1988) J Chem Phys 89:6128
17. Gruebele M, Zewail AH (1990) Physics Today, p 24, May
18. Merzbacher E (1970) Quantum Mechanics. Wiley, NY
19. Loudon R (1983) The quantum theory of light. Oxford Univ Press, Oxford
20. Taylor JR (1983) Scattering theory. Krieger, Malabar
21. Heller EJ, Sundberg RL, Tannor D (1982) J Phys Chem 86:1822
22. Shapiro M, Bersohn R (1982) Ann Rev Phys Chem 33:409
23. Brumer P, Shapiro M (1985) Adv Chem Phys 60:371
24. Henriksen NE (1988) Comments At Mol Phys 21:153
25. Brumer P, Shapiro M (1989) Chem Phys 139:221
26. Tannor DJ, Heller EJ (1982) J Chem Phys 77:202
27. Wigner EP (1932) Phys Rev 40:749
28. Heller EJ (1976) J Chem Phys 65:1789
29. Dahl JP (1983) in: Hinze J (ed) Energy storage and redistribution in molecules. Plenum Press, NY
30. Henriksen NE, Engel V, Schinke R (1987) J Chem Phys 86:6862
31. Henriksen NE, Billing GD, Hansen FY (1988) Chem Phys Letters 149:397
32. Heller EJ (1978) J Chem Phys 68:2066
33. Goursaud S, Sizun M, Fiquet-Fayard F (1976) J Chem Phys 65:5453
34. Engel V, Schinke R (1988) J Chem Phys 88:6831