

Photodissociation cross section for the lithium dimer Time-dependent method

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Introduction

During the last 20 years, the physics of dilute gases has seen major advances in two fields: laser cooling of atomic and molecular samples and femtosecond chemistry. In both cases, a strong motivation is to use laser light in order to achieve a better control of the system by reducing the energy distribution of the various degrees of freedom. In this context, two fundamental processes, i.e., photoassociation and photodissociation, or in other words formation and breaking of the chemical bond, have motivated a lot of theoretical and experimental studies. Photodissociation of diatomic and small polyatomic molecules is an ideal field for investigating molecular dynamics at a high level of precision [1]. In this poster we present the exemplary theoretical description of the photodissociation process. In Figure 1 we show the scheme of direct photodissociation using previously calculated adiabatic potential energy curves of the lithium dimer [2]. The initial $1^3\Sigma_u^+$ state and final $1^3\Pi_g$ state were performed by means of the MOLPRO [3] program package.

Photodissociation scheme

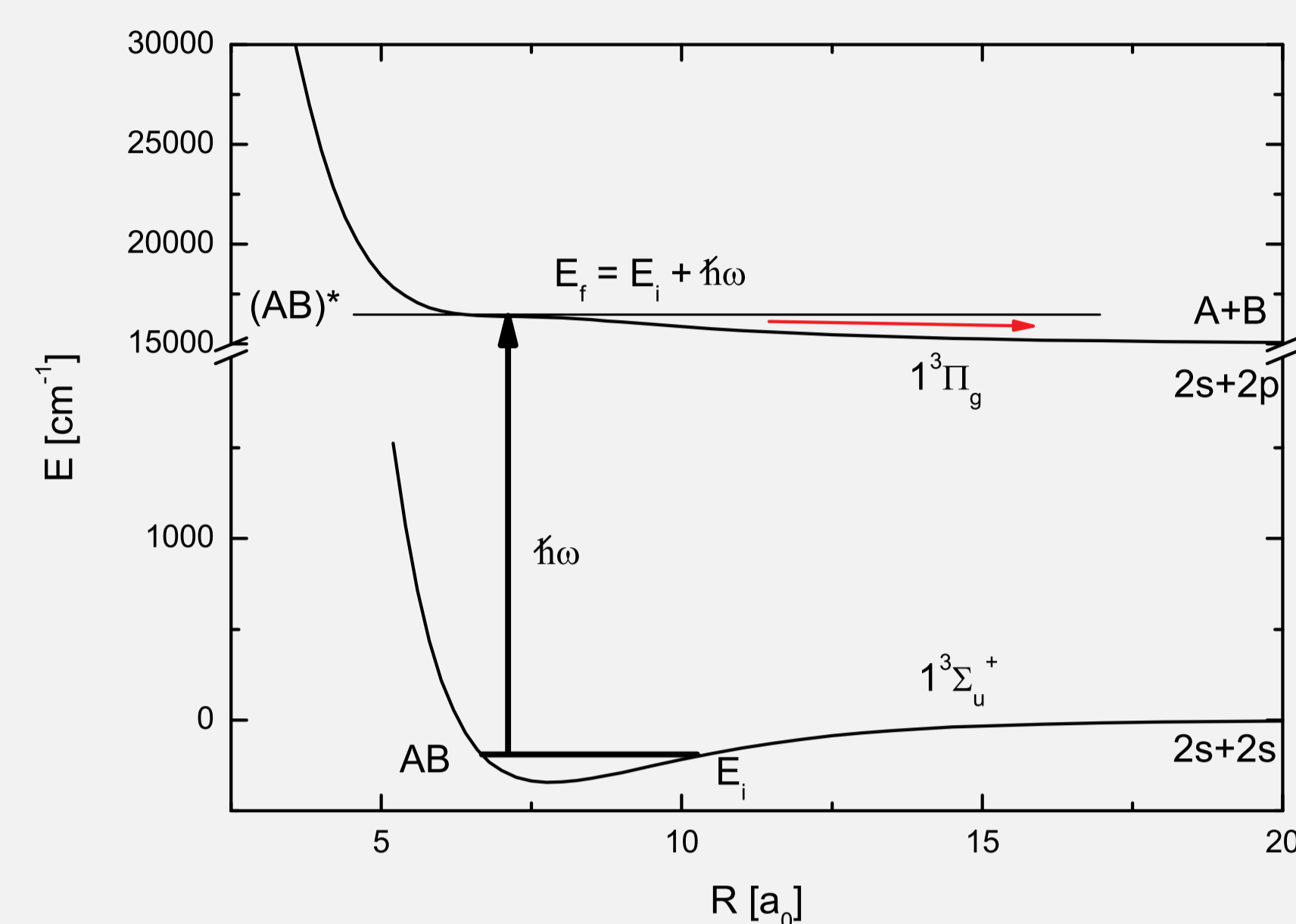


Figure 1. The single UV photon direct photodissociation scheme. The photon creates a single quantum state in the upper electronic state.

Photodissociation cross section

Below we present the procedure for calculations of photodissociation cross section in bound-free transitions (i - initial state, f - final state) [1]:

- the adiabatic potential energy curves $E_i^e(R)$ and $E_f^e(R)$ for the electronic states between which the transition occurs,
- the electronic transition dipole moment function $\vec{\mu}_{ij}^e(R)$,
- the nuclear wavefunctions $\Psi_i^{nuc}(R)$ and $\Psi_f^{nuc}(R)$,
- the photodissociation amplitude $t_{fi} = \langle \Psi_f^{nuc}(R) | \vec{\mu}_{ij}^e(R) \cdot \vec{e} | \Psi_i^{nuc}(R) \rangle$.

Following Schinke [1] or Balint-Kurti [4] photodissociation cross section may be given by expression

$$\sigma(\omega) = \frac{\rho\pi}{h\epsilon_0 c} E^{photom} |t_{fi}|^2, \quad (1)$$

where t_{fi} is the photodissociation amplitude, the factor $\rho = (2\pi\hbar)^{-1}$ is a constant and E^{photom} is the energy of the photon, provided that the energy in the upper electronic state is always taken as $E_f = E_i + E^{photom}$ [5].

Time-dependent method

We consider the time-dependent nuclear Schrödinger equation in the form

$$i\hbar \frac{\partial}{\partial t} \Phi_f(\vec{R}; t) = \hat{H}_{mol}(\vec{R}) \Phi_f(\vec{R}; t), \quad (2)$$

where $\Phi_f(\vec{R}; t)$ is a time-dependent wavepacket evolving on the adiabatic potential energy curve of the excited electronic state and $\hat{H}_{mol}(\vec{R})$ is the molecular hamiltonian. We can define the wavepacket as a coherent superposition of stationary states, each being multiplied by the time-evolution factor $e^{-iE_j^{mod}t/\hbar}$ [5, 6, 7]. The construction of the time-dependent wavepacket can be given as

$$\Phi_f(\vec{R}; t) = \int c_j(E_j^{mod}) e^{-iE_j^{mod}t/\hbar} \Psi_j^{nuc}(\vec{R}) dE_j^{mod}, \quad (3)$$

where $\Psi_j(\vec{R}; t)$ is a solution of (2) because each stationary wavefunction $\Psi_j^{nuc}(\vec{R})$ is an eigenfunction of $\hat{H}_{mol}(\vec{R})$ with the energy E_j^{mod} . In the next step we determine the initial condition in order to calculate coefficients $c_j(E_j^{mod})$ [1, 6].

$$\Phi_f(\vec{R}; t=0) = \vec{\mu}_{ij}^e(\vec{R}) \cdot \vec{e} \Psi_i^{nuc}(\vec{R}), \quad (4)$$

The initial condition informs us that the wavepacket at its start in the upper electronic state equals the wavefunction of the parent molecule, $\Psi_i^{nuc}(\vec{R})$, multiplied by the electronic transition dipole moment function $\vec{\mu}_{ij}^e(\vec{R})$. Using the equation (3) and the initial condition (4) we obtain the relation

$$c_j(E_j^{mod}) = \frac{1}{2\pi\hbar} \langle \Psi_j^{nuc}(\vec{R}) | \vec{\mu}_{ij}^e(\vec{R}) \cdot \vec{e} | \Psi_i^{nuc}(\vec{R}) \rangle = \frac{1}{2\pi\hbar} t_{fi}(E_j^{mod}), \quad (5)$$

where the photodissociation amplitude $t_{fi}(E_j^{mod})$ is defined above. Multiplying (3) from the left by $\Phi_f(\vec{R}; t=0)$ and integrating over all nuclear coordinates gives

$$S(t) \equiv \langle \Phi_f(\vec{R}; t=0) | \Phi_f(\vec{R}; t) \rangle = \frac{1}{2\pi\hbar} \int |t_{fi}(E_j^{mod})|^2 e^{-iE_j^{mod}t/\hbar} dE_j^{mod}, \quad (6)$$

where $S(t)$ is the autocorrelation function. Following Schinke [1] and the equation (1) yields the final expression for the total photodissociation cross section,

$$\sigma(E) = \frac{\rho\pi}{h\epsilon_0 c} E^{photom} \int_{-\infty}^{+\infty} e^{iEt/\hbar} S(t) dt, \quad (7)$$

The formal solution of the time-dependent Schrödinger equation (2) is given by

$$\Phi_f(\vec{R}; t) = e^{-i\hat{H}_{mol}(\vec{R})t/\hbar} \Phi_f(\vec{R}; t=0), \quad (8)$$

where $\Phi_f(\vec{R}; t=0)$ is the wavepacket at the start of the propagation process for $t=0$ and operator

$$\hat{U}(t) = \exp\left[-\frac{i\hat{H}_{mol}(\vec{R})t}{\hbar}\right], \quad (9)$$

is the time-evolution operator [7, 8, 9]. With (8) inserted into (6) and using the initial condition (4) the autocorrelation function becomes

$$S(t) = \langle \Phi_f(\vec{R}; t=0) | e^{-i\hat{H}_{mol}(\vec{R})t/\hbar} | \Phi_f(\vec{R}; t=0) \rangle = \langle \vec{\mu}_{ij}^e(\vec{R}) \cdot \vec{e} | \Psi_i^{nuc}(\vec{R}) | e^{-i\hat{H}_{mol}(\vec{R})t/\hbar} | \vec{\mu}_{ij}^e(\vec{R}) \cdot \vec{e} | \Psi_i^{nuc}(\vec{R}) \rangle. \quad (10)$$

In the beginning of the propagation, the wavepacket is constructed by the product of the nuclear wavefunction $\Psi_i^{nuc}(\vec{R})$ and the element of the electronic transition dipole moment function in the direction of the polarization of the electric field $\vec{\mu}_{ij}^e(\vec{R}) \cdot \vec{e}$. Using the split-operator method SPO, the time-evolution operator (9) is approximated by a symmetric splitting of the kinetic energy operator in the following way [6, 8, 9]

$$\hat{U}(t) = \exp\left[-\frac{i\hat{H}_{mol}(\vec{R})t}{\hbar}\right] \approx \exp\left[-\frac{i\hat{T}_{mol}(\vec{R})t}{2\hbar}\right] \exp\left[-\frac{i\hat{V}_{mol}(\vec{R})t}{\hbar}\right] \exp\left[-\frac{i\hat{T}_{mol}(\vec{R})t}{2\hbar}\right], \quad (11)$$

The propagation of the wavepacket involves the following steps: the Fourier transformation of the wavepacket to the momentum space, multiplying it by the free particle propagator $\exp(-i^2 t/4m\hbar)$ and transforming back to the coordinate space, where it is multiplied by $\exp(-iE_f^e(R)t/\hbar)$. The resulting function is Fourier transformed to the momentum space, multiplied by $\exp(-i^2 t/4m\hbar)$ and transformed again back to the coordinate space in order to complete one timestep propagation [6, 8, 9].

Photodissociation cross sections

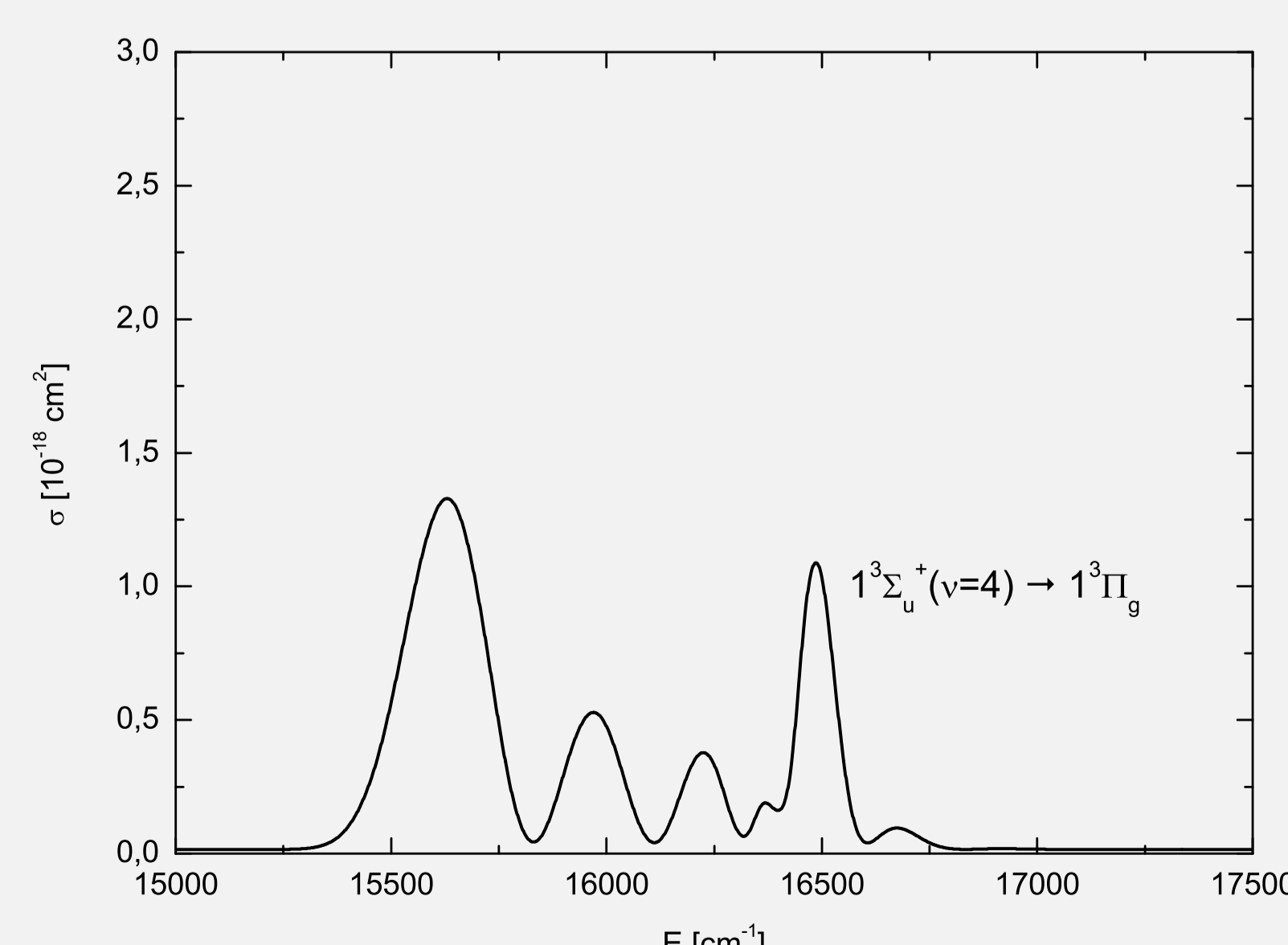
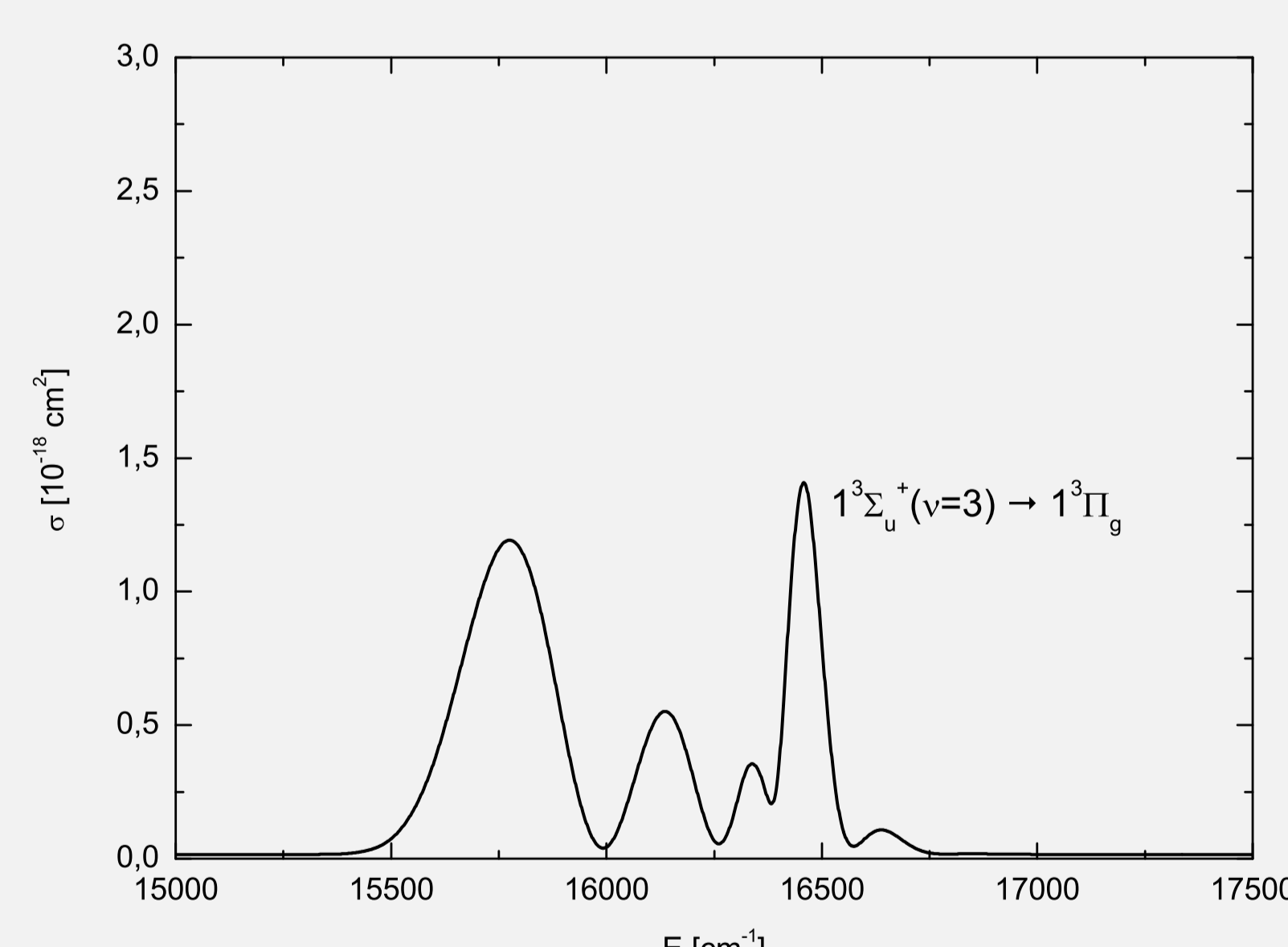
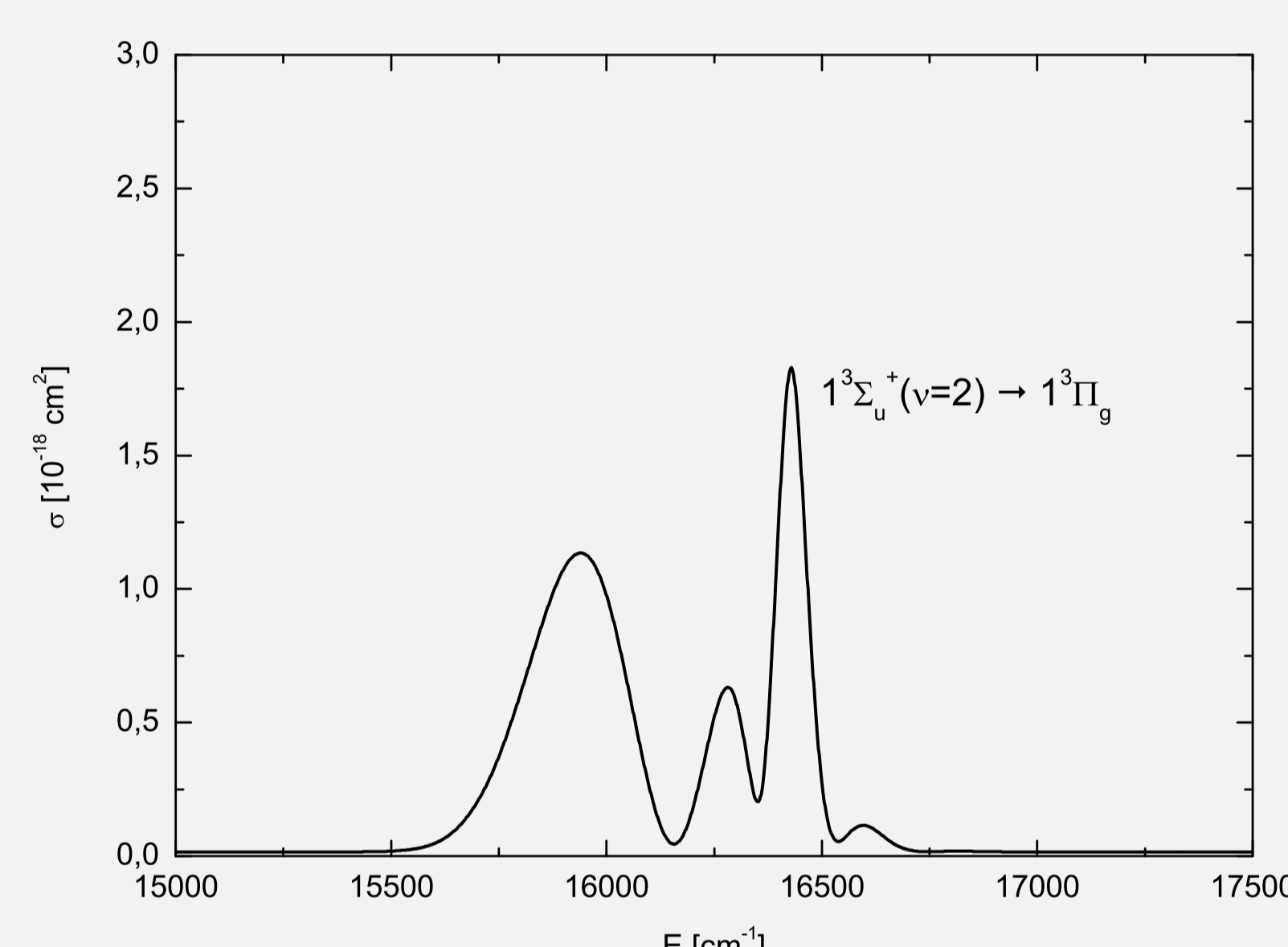
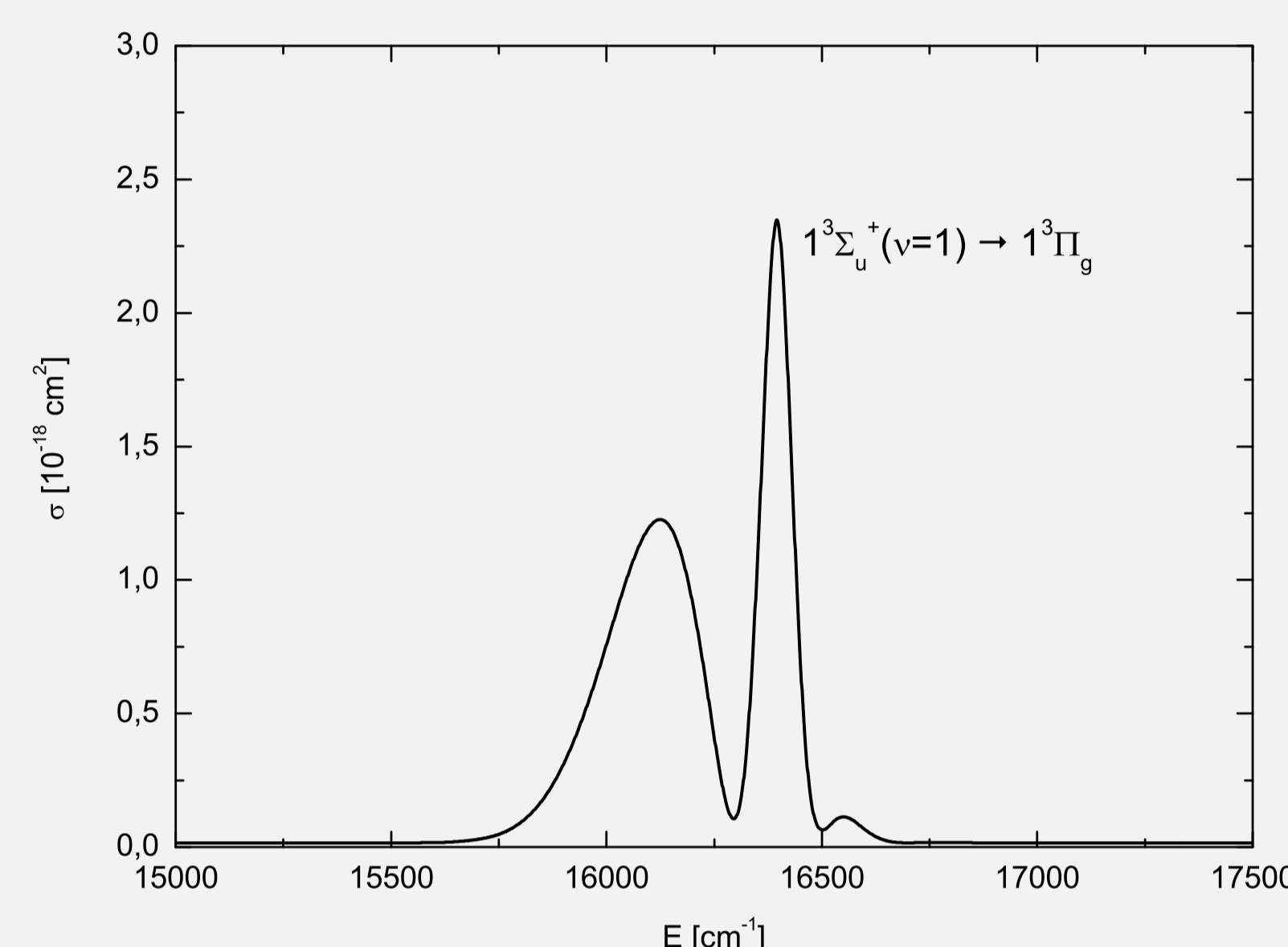
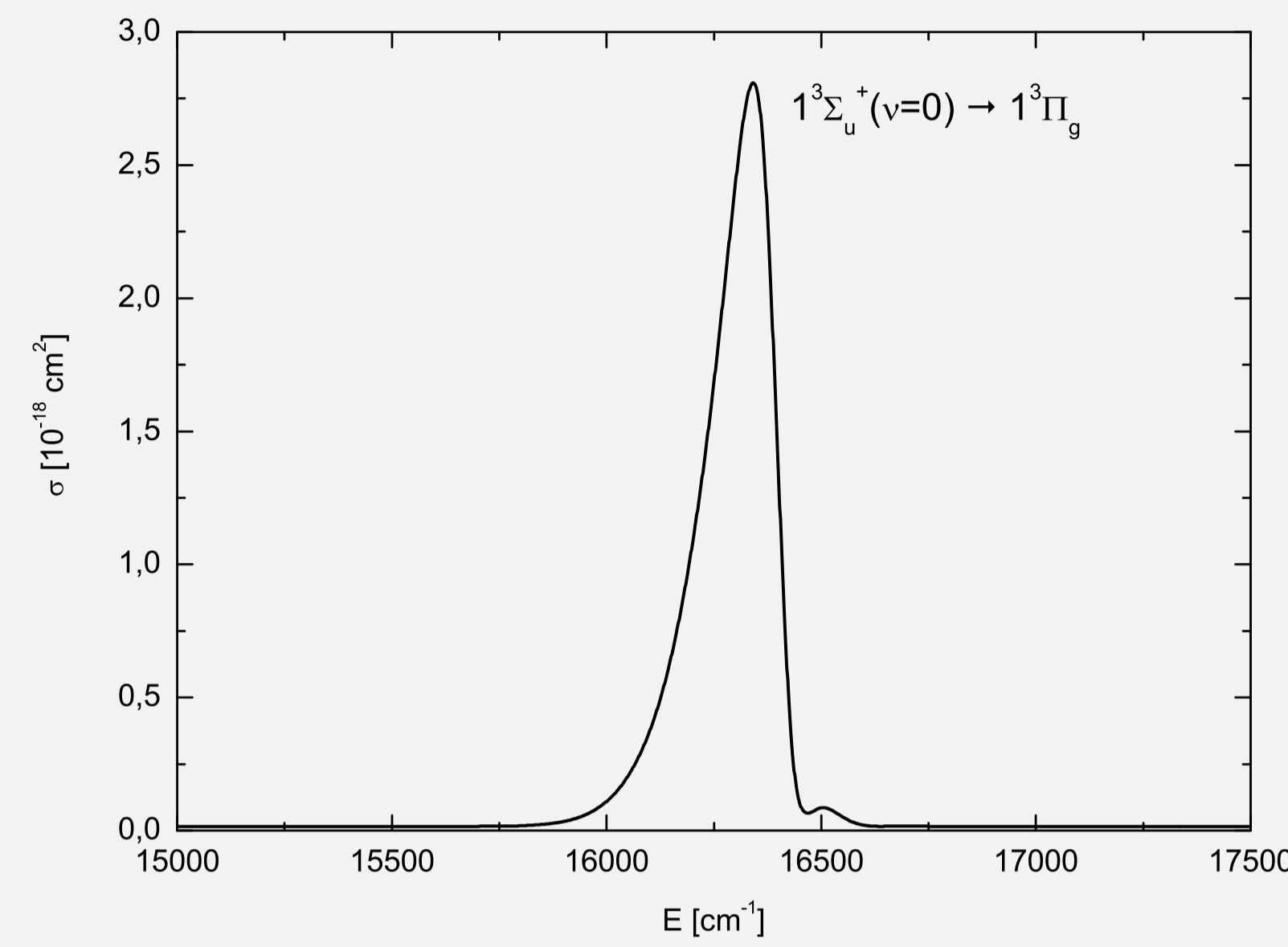


Figure 2. Photodissociation cross sections are calculated for transitions between the initial $1^3\Sigma_u^+$ ($\nu = 0, 1, 2, 3, 4$) states and the excited $1^3\Pi_g$ state.

Autocorrelation functions

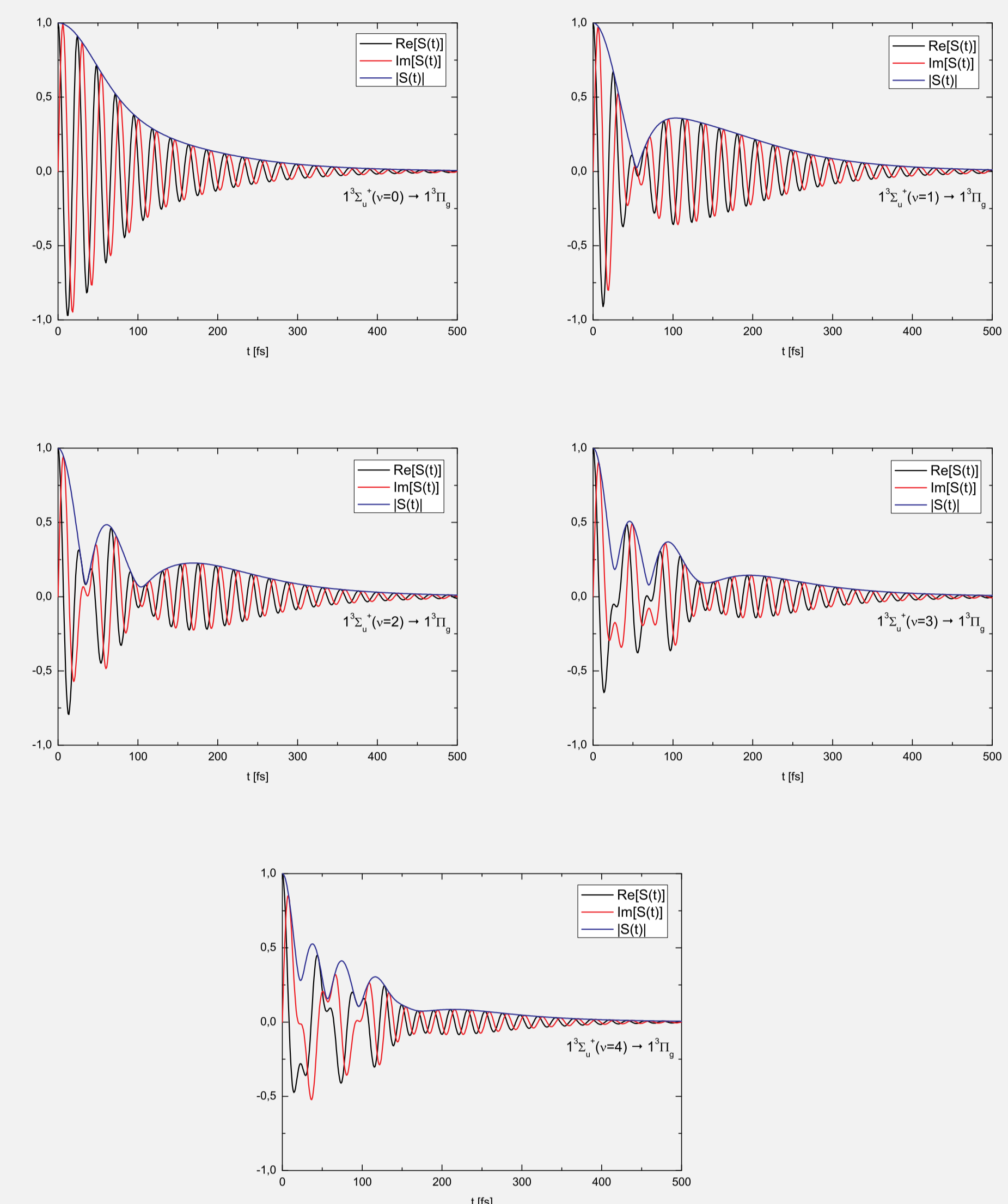


Figure 3. Autocorrelation functions in the considered photodissociation process.

Time-dependent wavefunction

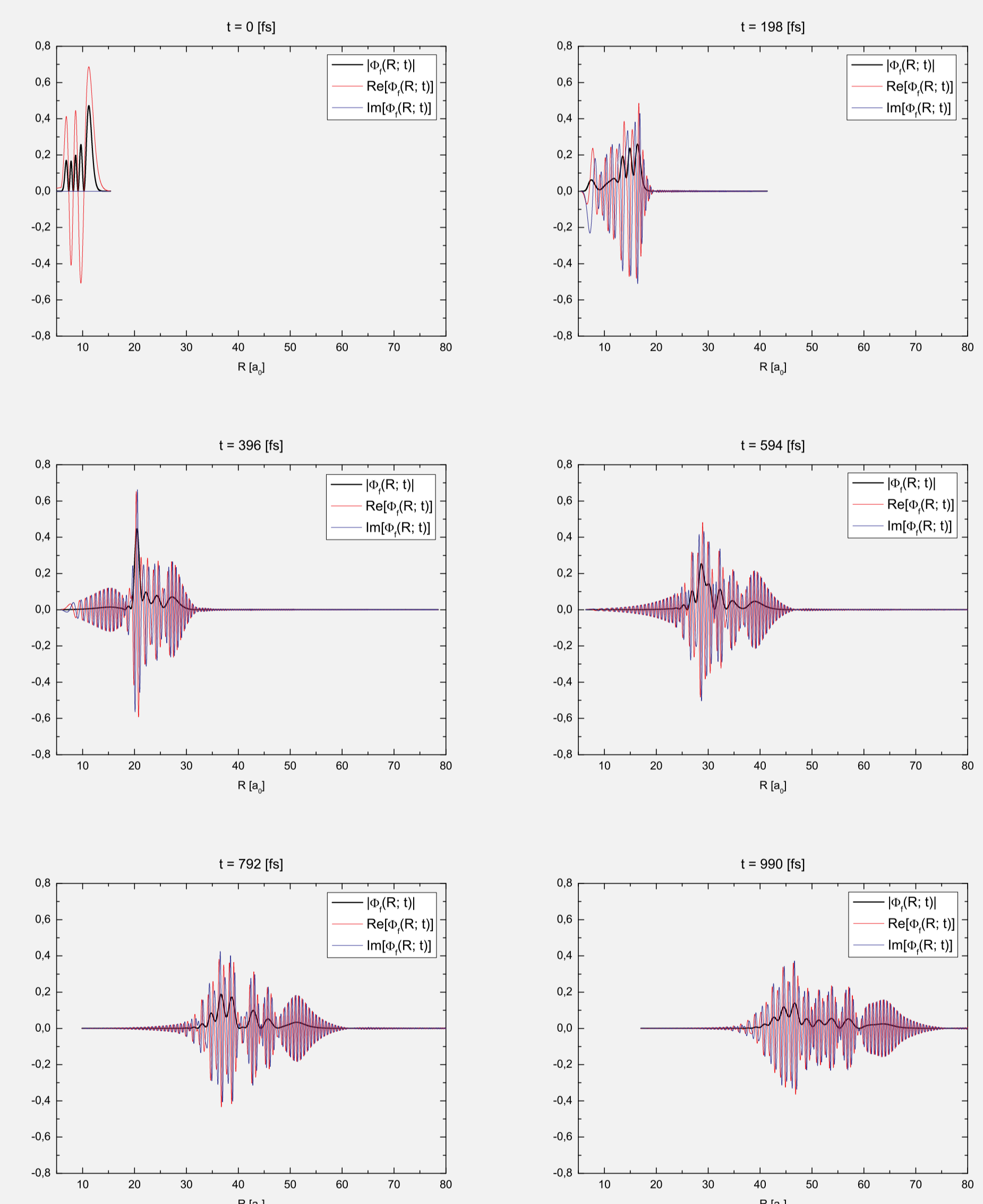


Figure 4. Evolution of the time-dependent wavefunction in the considered photodissociation process after transition between the initial $1^3\Sigma_u^+$ ($\nu = 4$) state and the excited $1^3\Pi_g$ state.

References

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