The Photodissociation/Recombination Dynamics of I₂ in an Ar Matrix: Wave Packet Propagation in a Mixed Quantum-Classical Picture

Udo Schmitt [a] and Jürgen Brickmann*

Physikalische Chemie I and Darmstädter Zentrum für Wissenschaftliches Rechnen; Technische Hochschule Darmstadt Petersenstr. 20, D-64287 Darmstadt, Germany (brick@pc.chemie.th-darmstadt.de)

[a] part of the Ph.D.-thesis of Udo Schmitt ,Technische Hochschule Darmstadt (D17).

Introduction

The theoretical description of photodissociation processes of molecules after short time laser excitations is essentially based on the formalism of quantum mechanics, i.e. both the product formation and the energy distribution are strongly related to the time evolution of a quantum wave packet. This time evolution can be treated within fully quantum dynamical concepts with reasonable computation effort only if a very small number of degrees of freedom are considered. The situation here is very similar to that of quantum scattering theory. Only very small isolated molecules or a small number of system coordinates can be treated. Large molecules or molecules in contact with their environment are out of the scope of fully quantum dynamical calculations. In this work we present the results of a mixed quantum-classical approach wherein one relevant degree of freedom is treated quantum dynamically while all the others follow the laws of classical dynamics. The model system is a iodine molecule imbedded in a solid argon matrix. The treatment of the combined dynamics follows a discrete time-reversible propagation scheme for mixed quantum-classical dynamics which has been published recently by the present authors [1]. The results of the simulations are visualized and presented as a time sequence of images.

The time dependent SCF approximation

A considerable simplification of the dynamics of a system with many degrees of freedom can be obtained by separating the total system into two parts, the "relevant system", which is treated quantum mechanically, and the "bath" degrees of freedom, which shall be well described by classical equations of motion. A possible realization of such hybrid methods is the quantum/classical time-dependent self-consistent field (Q/C TDSCF) ansatz suggested by Gerber, Ratner and coworkers [2]. Within the Q/C TDSCF approach the total system wave function is approximated as a product of wavefunctions for each set of co-ordinates. Furthermore, it is assumed that the probability distribution of the bath degrees of freedom remains "classical" in time, i.e. the corresponding part of the wave packet remains strongly localized in co-ordinate and momentum space. The total system dynamics is then controlled by a time-dependent Schrödinger equation for the relevant system and classical equations of motion for the bath degrees of freedom. The coupling between the two sets is represented by the parametric dependency of the system Hamiltonian on the bath coordinates and by the functional dependency of the effective classical potential in the system wavefunction.

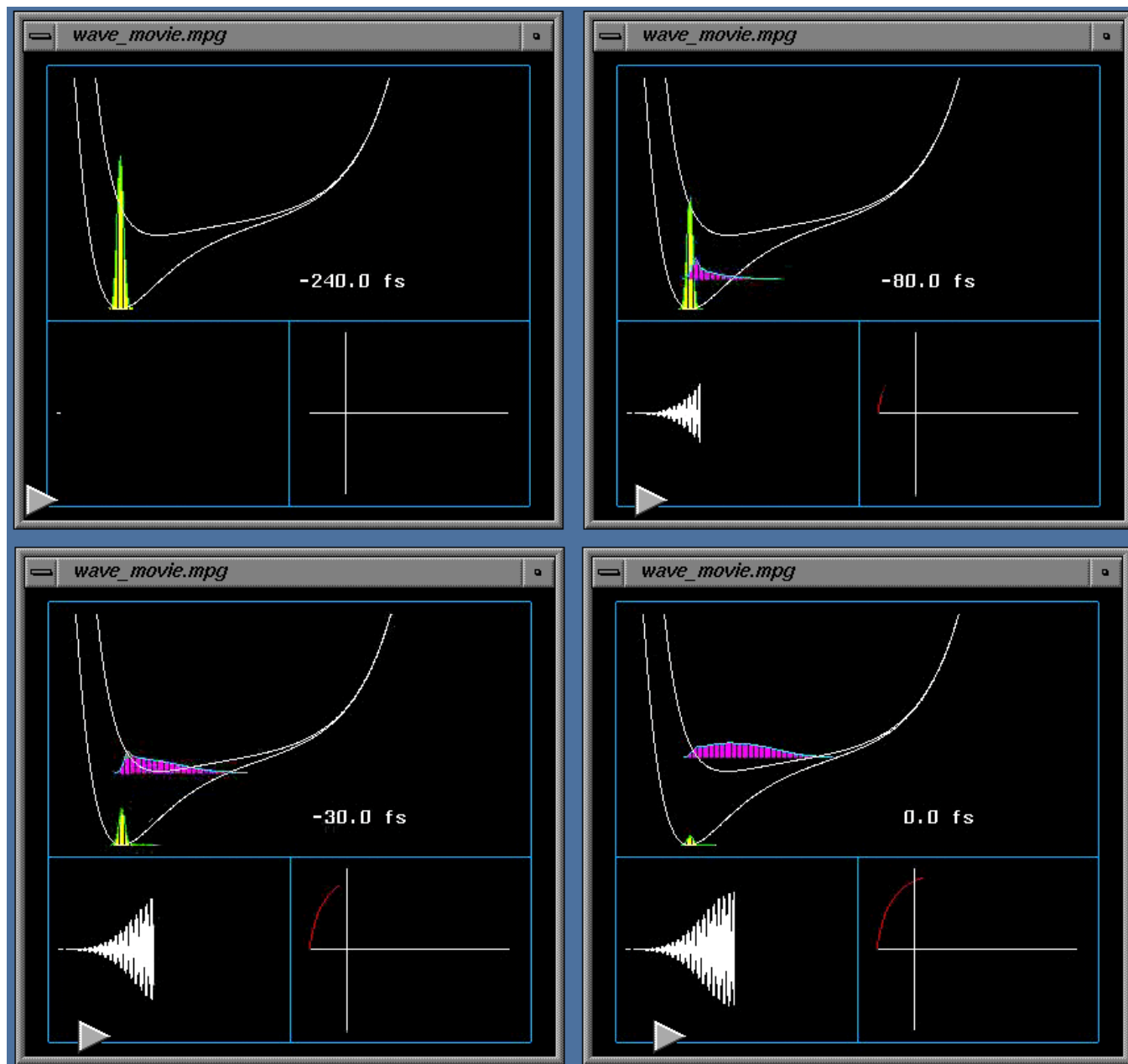** To whom correspondence should be addressed*

Figure 1. *Four individual scenes of the time sequences at time t = -240 fs, -80 fs, -30 fs and 0 fs.*

The discrete time propagation scheme

Intrinsic problems of the mixed mode propagation are related to the inherent time scale difference due to the large frequency disparity within both subsets. Using a single time scale for both, the quantum and classcial degrees of freedom, a very small time step is necessary for the description of the fast motion of the quantum modes. Consequently, such a procedure is time consuming and inefficient. This problem can be circumvented by the introduction of two different time steps for the quantum and classical modes,

respectively. A numerically stable multiple time step scheme has been suggested recently by the authors [1]. It is based on a reformation of the standard Q/C TDSCF equations of motion as a purely classical Hamilton-Jacobi type description by replacing the complex time-dependent co-efficients representing the quantum wave function by a linear combination of formal position and momentum co-ordinates. By grouping the formal position and momentum co-ordinates of the quantum part with the co-ordinates representing the classical subset into a new formal phase space [3], the time evolution can be described by a classical Liouville equation. The total system time evolution operator can be split off by using Trotter's formula [4,5], which then allows the introduction of a second, small time step for the integration of the quantum part. For a detailed dis-
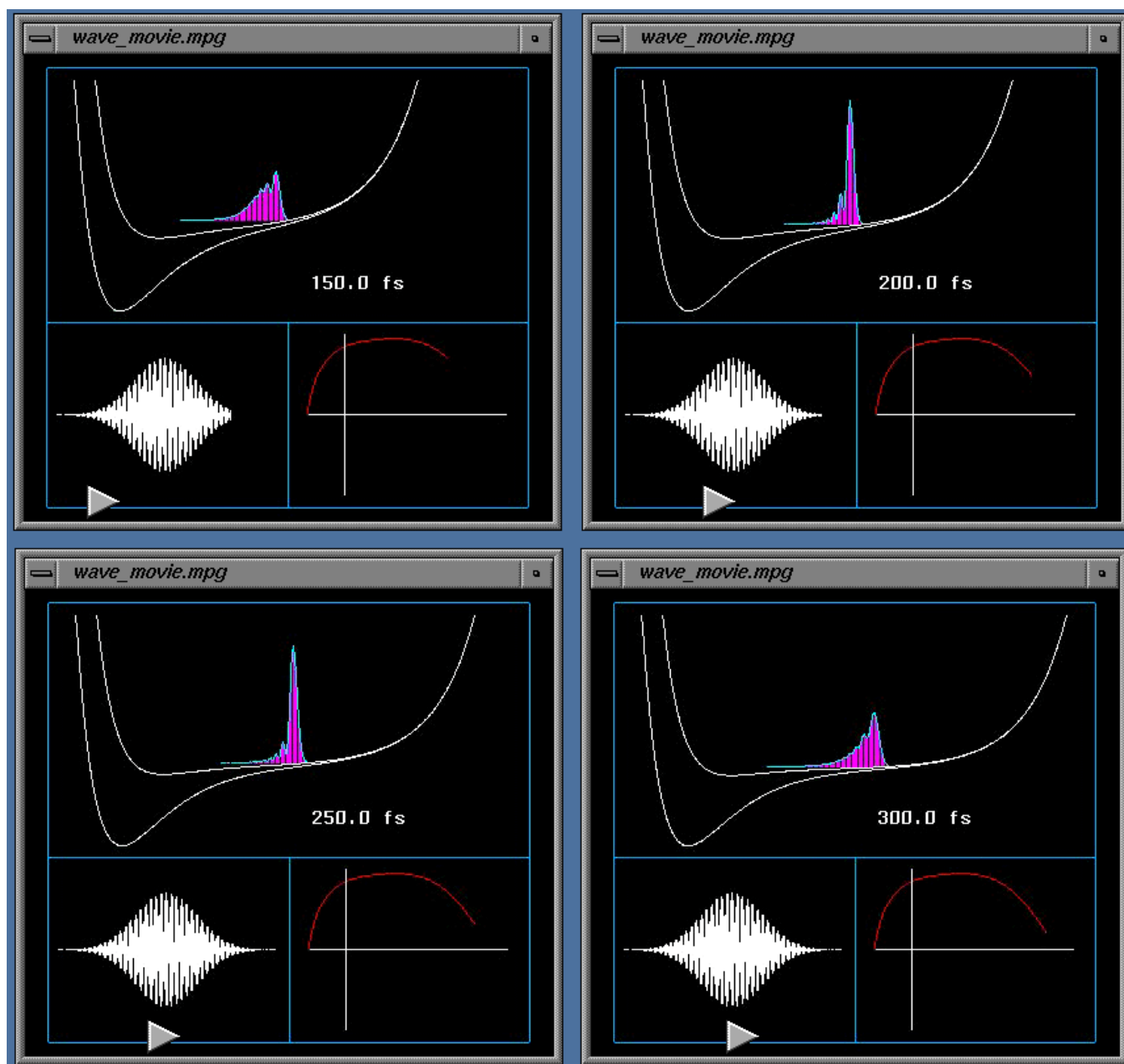
Figure 2. *Four individual scenes of the time sequences at time t = 150 fs, 200 fs, 250 fs and 300 fs.*

cussion see Ref. [1]. The resulting propagation scheme (reversible scheme, RPS) give rise to a significantly enhanced integration stability with respect to energy conservation, and rigorously accounts for time-reversibility due to the symmetric exponential factorization of the propagator.

The model system

We have applied the reversible propagation scheme (RPS) to simulate the photoexcitation process of I_2 immersed in a solid Ar matrix initiated by a femtosecond laser puls. The system serves as a prototypical model in experiment and theory for the understanding of photoinduced condensed phase chemical reactions and the accompanied phenomena like the cage effect and vibrational energy relaxation. The system/bath separation is introduced in the following manner:

The quantum subsystem is taken as the motion along the vibrational stretch co-ordinate of the I_2 molecule on two electronic surfaces, the ground state X and the excited state A, which are coupled through a transient off-diagonal interaction with a Gaussian shaped laser puls (τ=80 fs) with a carrier frequency of λ=728 nm. The wave function representing the I_2 stretch is expanded in a discrete coordinate representation using 256 equally spaced grid points

for each electronic state. The two electronic states are represented by Morse potentials with appropriate parameters. The I_2 is inserted into a double-substitional site of an Ar fcc-lattice, which is modelled by 498 classical Ar atoms placed in a cubic box employing periodic boundary conditions. The Ar-Ar and I-Ar intercations are described by pairwise additive Lennard-Jones potentials. The equations of motion are integrated within the RPS using a large time step $\Delta t=5$ fs for the classical system, and a small time step $\delta t=0.05$fs for the quantum part. In the classical part, the well-known velocity Verlet integrator is employed, whereas the quantum subsystem is integrated with an explicit symplectic partitioned Runge-Kutta of third order. A detailed description of the numerical implementation will be given elsewhere [6].

Wave packet visualization

The direct way of distributing the results of a dynamics calculation is the display of time sequences. Here we present two sequences, which are generated as it is shown in Figs. 1 and 2. Three different subwindows are generated: the upper part showing the electronic ground (lower curve) and the excited A state (upper curve) of the I_2 molecule potential surfaces, which are modified with respect to the gas-phase potential by the time-dependent meanfield Ar-I interaction resulting in a solvent cage repulsive wall for larger I-I separations. Furthermore, the time-dependent probability density of the I_2 stretch on the X (yellow) and the A state (purple) are depicted. A clock giving the time in femtoseconds is placed in the left part underneath the electronic states. In the lower part, the electric field amplitude representing the laser puls is shown as a function of time in the left corner, whereas in the right part the expectation values of the co-ordinate and momentum for the I_2 stretch are given in a phase space-like illustration. Therein, the time evolution is shown in a color-coded manner, starting with phase space points at t=–250 fs in red, and ending up with yellow at t=6750 fs. The time origin is chosen as t=–250 fs to obtain the maximum of the laser intensity at t=0 fs. The complete time evolution can be explored interactively and is attached as an electronic supplement.

Discussion

The complete time evolution of the wave packet can be studied by travelling along the time axis in both directions. Starting from a vibronic wave function respresenting the vibrational ground state on the lower electronic surface, the transient electric field intensity coupling the two electronic states induces a transition to the excited A state. Due to the strong repulsive character of the A state potential surface in the Frank-Condon regime, the resulting wave packet starts to move immediately towards larger I-I seperation. After t≈60 fs the laser pulse has almost completely populated the A state resulting in a broadened, approximately Gaussian shaped wave packet travelling towards the solvent cage wall. The collision of the wave packet with the repulsive solvent wall gives rise to a significant energy transfer to the nearest Ar atoms, which results in the solvent wall being pushed away. During that process, the wave-packet refocuses due to quantum interference of the incoming part of the wave-packet with the one already at the solvent wall reflected. While the solvent wall is moving outwards, the wave-packet, which has lost most of its kinetic energy, starts to delocalize along almost the whole I_2 stretch range. After t≈600 fs, the solvent wall starts moving backwards, kicking the delocalized wave packet, which results in an energy transfer back into the I_2 stretch vibration, causing the wave packet to travel towards shorter I-I separations. After being reflected at the inner repulsive wall of the A state, the fairly delocalized wave packet interacts with the solvent cage a second time, where the amount of energy being exchanged is noticable reduced compared to the first cage encounter.

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