HCl photodissociation on argon clusters: Effects of sequential solvation and librational preexcitation

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Abstract

Photolysis of the HCl molecule surface solvated on clusters with two to twelve argon atoms is investigated by means of quantum molecular dynamics simulations. Two basic questions are addressed: i) How does the cage effect change upon increasing the size of the cluster, and ii) How can caging be influenced by an IR excitation of HCl hindered rotation (libration) prior to UV photolysis. The efficiency of caging is discussed in terms of measurable quantities. In the time domain, temporary populations of the trapped hydrogen atom are monitored, while in the energy domain short-lived vibrational resonances are observed as a fine structure in the hydrogen kinetic energy distribution. While caging is negligible for the smallest clusters, it becomes more efficient upon increasing the cluster size, and for twelve solvent atoms the cage effect is already very strong. Finally, it is shown that while in the ground state the hydrogen atom points essentially towards the rare gas cluster, in excited librational states hydrogen is directed mostly away from argon atoms. As a consequence, caging of the photodissociating hydrogen atom in the case of a surface solvated HCl molecule can be efficiently "turned off" by librational preexcitation.

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I. Introduction

The ability of an inert solvent to hinder photodissociation of a solute molecule has been known for a long time.[1] While originally described in the condensed phase, this cage effect has been recently intensely studied also in system with a finite number of particles. Novel techniques for size-selection of neutral clusters prepared by supersonic expansion,[2–4] as well as progress in computational methods[5] have made it possible to investigate caging as a function of the number of solvent particles. By studying the influence of sequential solvation on photolysis of small molecules one can bridge direct photodissociation of an isolated chromophore on one side with condensed phase cage effect on the other side. Answers to the following questions can be obtained: What is the minimum number of solvent atoms for observable caging, how does caging depend on solvation site and vibrational/rotational state of the chromophore, and at what cluster sizes does the cage effect approach bulk values.

Among the most intensely studied systems of this type are rare gas clusters with a single hydrogen halide molecule. Numerous investigations have been devoted to the photolysis of HX (X=F, Cl, or Br) molecules with just one or two argon atoms as a solvent.[6–14] A bottom line of the above works is that a single rare gas atom is rather inefficient in hindering the highly energetic and delocalized photodissociating hydrogen atom. On the other end of system sizes, photolysis of an HX molecule embedded in or on large argon clusters with twelve or more rare gas atoms has been investigated in considerable detail,[15–18] with the conclusion that caging in these systems is significant and eventually approaches the effect of a rare gas matrix.[19–22] One of the goals of the present paper is to connect the case of a very weak caging by a single rare gas atom with large clusters as efficient cages. This is achieved by studying the effect of sequential solvation by two to twelve argon atoms on a photodissociating HCl molecule.

A typical feature of cryogenic mixed hydrogen halide–rare gas clusters is a large amplitude motion of the hydrogen atom perpendicular to the HX molecular axis. In a shallow intermolecular potential the light and cold hydrogen atom behaves as a strongly delocalized quantum particle. As a result, a fully solvated HCl molecule in rare gas matrices or large clusters practically freely rotates.[18,23] In the case of surface solvated $HCl(Ar)_n$ isomers, which are energetically preferred (or represents the only possibility) in smaller clusters,[24] the hydrogen motion is more hindered and the HCl molecule librates.[25–33] In our recent work, we have shown that rotational preexcitation strongly influences the photodissociation process of an HCl molecule embedded in the first solvation shell of twelve argon atoms.[18] Here, we among others demonstrate that photolysis and caging of a surface solvated HCl molecule, which is actually the most stable isomer of the $HCl(Ar)_{12}$ complex,[24] can be efficiently controlled by librational preexcitation.

The rest of the paper is organized as follows. In Section II we describe the systems under investigation and the relevant potentials. Methods used for the construction of the initial quantum states of the system and for the photodissociciation dynamics are reviewed in Section III. Section IV contains results and discussion, while concluding remarks are presented in Section V.

II. Systems and Potentials

Geometries of $HCl(Ar)_n$ (n=1,...,12) clusters in ground electronic and vibrational states have been determined recently.[24] In all cases, the most stable isomer corresponds to a surface solvated HCl molecule with the hydrogen atom pointing towards the argons. Inner solvation is disfavored even for the largest $HCl(Ar)_{12}$ where the fully solvated isomer lies some 150 cm^{-1} above the energetically lowest structure,[24] since the HCl molecule is slightly too large to fit into the argon cage. In this study, we have considered for each cluster size the most stable structure for the construction of the initial vibrational wavefunction.

The ground electronic state potential is constructed from an accurate three-body potential for the HCl-Ar interaction,[34] using pair potentials for the remaining interactions. The ground state H-Cl potential is approximated by a Morse curve[35] and the HFD-B potential is adopted for the argon-argon interaction.[36]

The photodissociation dynamics is initiated by promoting the HCl molecule from a bound $^1\Sigma$ state to a strongly repulsive $^1\Pi$ state[37] by a very short UV pulse. The potential energy surface in the electronically excited state is constructed via a Diatomics-in-Molecule Hamiltonian[19] which explicitly accounts for the anisotropy of the chlorine-argon interaction.[38] The following additional diatomic potentials serve as an input: The H-Cl and H-Ar potentials are taken from *ab initio* calculations[18,39] and the Ar-Ar potential is the same as in the ground state.

As in our previous study,[18] we constrain ourselves for the sake of feasibility of quantum dynamical calculations to an approximation which neglects the effects of the Cl atom spin-orbit coupling and of non-adiabatic transitions. While these effects are found to play a role in longer time photodissociation dynamics of the HCl molecule in very large argon clusters and matrices,[15,16,19] their influence is minor in smaller clusters especially if the emphasis is on the early dynamics following the photoexcitation event.[18]

III. Method

A. Initial state of the system

Clusters prepared by supersonic jet expansion into the vacuum have very low temperatures (typically few Kelvins) where quantum effects can play an important role. At the same time, the systems under study are initially close to their ground vibrational state and the heavy atoms (chlorine and argons) can be treated in the harmonic approximation. As in our previous study,[18] we employ for the description of these cage modes normal coordinates and Gaussian wavefunctions. While similar arguments apply also for the H-Cl vibration in the electronic ground state, the delocalized hydrogen libration is clearly non-harmonic and has to be treated more carefully. We have found that a truncated expansion into symmetry adapted spherical harmonics very efficiently and accurately describes this delocalized motion.[18]

The initial wavefunction Ψ_0 of the $HCl(Ar)_n$ system in the electronic ground state is constructed as follows:[18]

$$\Psi_0(q_1,...,q_{3n-3},\rho,\phi,\theta) \propto e^{(-\frac{1}{2}\omega_1 {q_1}^2)}...e^{(-\frac{1}{2}\omega_{3n-3} {q_{3n-3}}^2)}\frac{\Phi_{vib}(\rho)}{\rho}\Phi_{lib}(\phi,\theta) \qquad (1)$$

where q_i are the $3n-3$ normal coordinates, ρ,ϕ,θ are internal spherical coordinates of the HCl molecule, and ω_i are the harmonic frequencies of the cage modes. The harmonic ground state vibrational wavefunction Φ_{vib} of the HCl molecule is divided by ρ, which comes from the use of spherical coordinates. The initial librational wavefunction Φ_{lib} of the HCl molecule, which corresponds either to the lowest or to excited librational states, has been obtained as a solution of the corresponding time-independent Schrödinger equation using an expansion into spherical harmonics.[18]

B. Quantum dynamics

On one hand a numerically exact quantum mechanical treatment of the dynamics of the systems under study is, except for the smallest clusters, beyond present computational means, on the other hand rather dramatic approximations are well justified. The early photodissociation dynamics concerns primarily the light and energetic hydrogen atom which has to be treated properly as a three-dimensional quantum particle. The heavy atoms, however, hardly start to respond to the hydrogen motion on the relevant sub-100 fs timescale. Since in this study we are primarily interested in the ultrafast hydrogen motion we can treat the influence of the heavy atoms on the hydrogen motion in a mean-field approximation, using the Classical Separable Potential method.[40] The employed computational methods have been described and justified in an exhaustive way in our recent study.[18] In the following, we present computational details concentrating on minor differences from the previous work.

The three-dimensional hydrogen wavefunction is discretized on a 3D Cartesian grid. The mean excess energy of the photodissociating hydrogen is more than 3 eV, therefore, the number of grid points has to be relatively large. A grid of $200\times200\times200$ points has been employed. A cubic optical potential has been added far enough from the reactive region in order to absorb the outgoing parts of the hydrogen wavefunction. The interaction between the cage and the hydrogen atom has been accounted for within a mean-field approach.[18] The center of mass of the HCl molecule has been assumed to coincide with the chlorine atom, which has been kept frozen during the simulation. In this way, errors caused by the non-separability of the relative hydrogen and chlorine motions in the Franck-Condon region have been practically canceled out in a simple way.

For the construction of the effective Classical Separable Potentials[40] 150 auxiliary Wigner trajectories have been employed. This number of trajectories results in effective potentials which almost preserve the symmetry of the system under study. In order to achieve perfect symmetry, the CSP potentials have been symmetrized *ex post* by applying all allowed symmetry operations and by a consequent averaging. The relevant point groups for the particular clusters are C_{2v} for $HClAr_2$, C_{3v} for $HClAr_3$, C_{2v} for $HClAr_4$, C_{4v} for $HClAr_5$, C_{5v} for $HClAr_6$, and C_{5v} for $HClAr_{12}$. Finally, the split propagator[41] with a time step of 0.025 fs has been used for wavefunction propagations and the action of the kinetic energy operator has been evaluated using a fast Fourier transform algorithm.[42,43]

IV. Results and Discussion

A. Initial Librational Wavefunctions

Librational wavefunctions corresponding to the HCl molecule solvated on clusters with two to twelve argon atoms are depicted in Figs. 1 and 2. Diffuse structures represent the librating hydrogen, while wired spheres are the chlorine and argon atoms. High density of dots corresponds to a high probability of the occurrence of the hydrogen atom, while low density indicates low probability and/or nodes on the librational wavefunction. The size of the heavy atom spheres corresponds to regions in space inaccessible to a photodissociating hydrogen with a mean excess energy of 3.5 eV.[18,39] Finally, the reported relative energies are given with respect to the corresponding ground librational state.

Figs. 1 and 2 provide a unified view on the effect of sequential solvation on hydrogen libration starting from two solvent atoms, studied already earlier,[27,30,31] to relatively large clusters. In all cases, the ground librational state is characterized by a large amplitude bending motion with the hydrogen atom pointing essentially towards the argons. For such geometries the photodissociating hydrogen maximizes its interaction with the argons and caging can be expected to be most pronounced. Nevertheless, as will be shown later, only for larger clusters the cage effect is strong enough to be directly observable. Interestingly, in all clusters there exist low-lying excited librational states, where most of the hydrogen wavefunction is oriented away from the cluster or at least sidewise. This is demonstrated in Fig. 2 for the case of the $HCl(Ar)_{12}$ complex. For these excited librational states caging becomes inefficient since the photodissociating hydrogen minimizes the interaction with the argon cage. In other words, librational preexcitation can be used to "turn off" the cage effect for surface solvated hydrogen halides.

Out of the systems under study, clusters with three, five, six and twelve atoms possess higher symmetries having more than a twofold rotational axis. As a result doubly degenerate librational states occur in these complexes. In Fig. 2 one of the possible representations of these degenerate states in the $HCl(Ar)_{12}$ cluster is displayed, however, any linear combination of these functions is also valid.

B. Photodissociation Dynamics

Unlike in the gas phase, where the photodissociation process is direct, bifurcations of the hydrogen wavefunction caused by collisions with solvent atoms are observed upon HCl photolysis in argon clusters. The relative importance of these collisions strongly depends on the size of the cluster. This can be seen from Fig. 3 which depicts time evolution of the hydrogen radial probability distributions[18] for clusters with two to six argons. The intensity of the dots in Fig. 3 corresponds to the square of the hydrogen wavefunction at a given time and distance from the chlorine atom, integrated over the two angular coordinates. For the smallest clusters, direct dissociation during which the hydrogen monotonously flies away from the cluster region dominates and only weak bifurcations occur during the first 25 fs. In this sense, the photodissociation dynamics in $HCl(Ar)_n$ $(n \leq 4)$ does not differ significantly from that in the gas phase or in Ar...HCl.[9,11,12] Caging in these clusters is very weak and causes only a negligible prolongation of the time spent in the interaction region, compared to the free HCl molecule. However, starting with five argon atoms caging rapidly increases. Fig. 3 demonstrates that also for the larger clusters direct dissociation is a dominant process. In other words, most of the hydrogen probability flux leaves the cluster area right after the first interaction with the argons around 10 fs after photoexcitation. However, for clusters with more than four argons a much more significant portion of the flux remains temporarily in the cluster region and strong bifurcations occur for up to 40 fs. This is caused by the structures of the Ar_5 and larger cages, where a compact solvation half-shell develops opposite to the dissociating hydrogen. An important role is played by an argon atom which undergoes a direct head-on collision for the most probably hydrogen angular orientation. Such a cage atom appears for the first time in the $HCl(Ar)_5$ cluster.

Fig. 4 depicts time evolution of the hydrogen radial probability for the case of photolyzed HCl molecule surface solvated on the Ar_{12} cluster. A strong cage effect with multiple bifurcations is clearly seen on Fig. 4a, which corresponds to photodissociation initiated from the ground librational state with the hydrogen atom pointing towards the cluster (see Fig. 2a). The major part of the hydrogen probability flux is deflected by the first two layers of argon atoms and there is only a negligible probability of direct (collisionless) dissociation through the cage. Three pronounced recurrences shown in Fig. 4a demonstrate repeated collisions of hydrogen with the cluster. The situation becomes dramatically different for photolysis started from the first non-degenerate librationally excited state. In this state most of the initial hydrogen density is oriented sidewise with respect to the cage (see Fig. 2b). As a results caging becomes very inefficient and, consequently only a single recurrence occurs during the dynamics. Thus, librational preexcitation can serve as a switch for efficiently 'turning off' the cage effect.

C. Observable Quantities

Caging results in observable effects both in the time and energy domains. A time-dependent property, which is in principle measurable in a pump-probe experiment, is the temporary population of the hydrogen in the cluster.[18] In our simulations this populations has been calculated as a time-dependent integral of the hydrogen wave function over the cluster region, defined as a sphere of a radius of 4 Å centered in the Cl atom. Fig. 5 depicts the hydrogen populations temporarily trapped in clusters with two to six argon atoms. The smallest clusters practically do not slow down the exiting hydrogen atom and the temporary population rapidly decays to zero. Larger clusters, however, are able to partially hinder the hydrogen wavefunction and as a results the population decay is slower indicating a delayed cage exit and temporary trapping. The decay of the hydrogen population in the cluster region is, among the systems under study, slowest for the librationally cold $HCl(Ar)_{12}$ cluster. However, a definition of a cluster region differs for the small and the largest system, therefore, it is hard to quantitatively compare the corresponding population decays.

An energy domain experimental observable which directly reflects the effect of caging is the final kinetic energy distribution (KED) of the hydrogen atom. From our simulations, KED is evaluated as the Fourier transform of the hydrogen autocorrelation function.[11,12,14,18] The KED spectra for $HCl(Ar)_n$ (n=2-6) clusters are depicted in Fig. 6. While for two solvent atoms the KED spectrum is practically structureless and very similar to that of Ar...HCl and free HCl,[11] a gradual rise of structural features is observed upon enlarging the cluster size. These structures in the KED spectra correspond to very short-lived vibrational resonances of the dissociating hydrogen in the solvent cage with a sub-60 fs lifetime and period of 20 fs.[18]

Fig. 7 shows the KED spectra for HCl photolysis on the Ar_{12} cluster initiated either from the ground or from the first non-degenerate excited librational state. In the former case strong caging results in a well developed vibrational structure in the KED. This means that a significant part of the hydrogen wavefunction lives for nearly 100 fs in the cage and repeatedly returns to the Franck-Condon region. Clearly, the resonant structure is the strongest among the systems under study. It is even stronger than in the case of a rotationally cold photodissociating HCl molecule fully solvated in the Ar_{12} cluster.[18] On the other hand, the structure in the KED disappears upon librational preexcitation, which orients most of the photodissociating hydrogen away from the argon cluster.

For the possible experimental realization of librational control it is important to take into account energy considerations. Our calculations as well as previous studies[26] show that the level spacing between the ground and lowest excited librational state amounts to 35-70 cm^{-1}. Thus, for efficient discrimination between the librational states the cluster temperature should not exceed few tens of Kelvins. This is realistic for the cluster sizes investigated here. For larger clusters, where higher temperatures might cause a problem, the technique of embedding in helium droplets, which leads to a very efficient cooling, could in principle be employed. Another point is which experimental observable should be used as a fingerprint of the librational control mechanism. Here, we suggest to monitor the disappearance of the resonant structure in the hydrogen KED upon librational preexcitation. The present setup corresponds to an ultrashort (therefore, energetically broad) exciting UV pulse. Another option is to use a longer (nanosecond) pulse with a frequency at the low energy tail of the hydrogen halide absorption band. Such an excitation produces a much less energetic hydrogen, which is more efficiently trapped in the argon cage. An observable consequence of librational preexcitation is then a disappearing low energy part of the KED, corresponding to caged hydrogens. For the case of hydrogen bromide on argon clusters, this possibility is discussed in our subsequent paper.[44]

V. Conclusions

Effects of sequential solvation and librational preexcitation on the photolysis of hydrogen chloride on clusters with two to twelve argon atoms have been studied using quantum molecular dynamics simulations. While the smallest clusters are inefficient in caging, it has been shown that the cage effect becomes gradually stronger upon enlarging the cluster size and it becomes clearly observable e.g., in the kinetic energy distribution of the dissociating hydrogen. Among the systems under study, the strongest cage effect has been observed in the $HCl(Ar)_{12}$ cluster. It has been shown, that caging in this cluster is even more efficient than in its fully solvated isomer. Finally, a novel effect has been demonstrated for the largest cluster, namely that caging for surface solvated hydrogen containing molecules can be efficiently "turned off" by an IR librational excitation prior to the UV photolysis. A measurable signature of this effect is the disappearance of the resonant structure in the hydrogen kinetic energy distribution upon librational preexcitation.

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References

1. J. Franck and E. Rabinovitch, Trans. Far. Soc., **30**, 120 (1934).
2. U. Buck and I. Ettischer, J. Chem. Phys., **108**, 33 (1998).
3. U. Buck and I. Ettischer, Chem. Phys. Lett., **269**, 321 (1997).
4. T. A. Beu, U. Buck, I. Ettisher, M. Hobein, J. G. Siebers, and R. J. Wheatley, J. Chem. Phys., **106**, 6806 (1997).
5. P. Jungwirth and R. B. Gerber, Chem. Rev., **99**, 1583 (1999).
6. A. Garcia-Vela, R. B. Gerber, D. G. Imre, and J. J. Valentini, Phys. Rev. Lett., **71**, 931 (1993).
7. A. Garcia-Vela, R. B. Gerber, and U. Buck, J. Phys. Chem., **98**, 3518 (1994).
8. A. Garcia-Vela and R. B. Gerber, J. Chem. Phys., **103**, 3463 (1995).
9. A. Garcia-Vela, J. Chem. Phys., **108**, 5755 (1998).
10. J. Segall, Y. Wen, R. Singer, C. Wittig, A. Garcia-Vela, and R. B. Gerber, Chem. Phys. Lett., **207**, 504 (1993).
11. T. Schroeder, R. Schinke, M. Mandziuk, and Z. Bacic, J. Chem. Phys., **100**, 7239 (1994).
12. T. Schroeder, R. Schinke, and Z. Bacic, Chem. Phys. Lett., **235**, 316 (1995).
13. E. Narevicius, D. Neuhauser, H. J. Korsch, and N. Moiseyev, Chem. Phys. Lett., **276**, 250 (1997).
14. M. Monnerville and B. Pouilly, Chem. Phys. Lett., **294**(6), 473–479.
15. M. Niv, A. I. Krylov, and R. B. Gerber, Faraday Discussions, **108**, 243 (1997).
16. M. Niv, A. I. Krylov, R. B. Gerber, and U. Buck, J. Chem. Phys., **110**, 11047 (1999).
17. B. Schmidt, Chem. Phys. Lett., **301**, 207 (1999).
18. P. Zdanska, B. Schmidt, and P. Jungwirth, J. Chem. Phys., **110**, 6246 (1999).
19. A. I. Krylov and R. B. Gerber, J. Chem. Phys., **106**, 6574 (1997).
20. J. Manz, B. Schmidt, and P. Saalfrank, J. Chem. Soc. Faraday Trans., **93**, 957 (1997).
21. I. H. Gersonde and H. Gabriel, J. Chem. Phys., **98**, 2094 (1993).
22. F. Neugebauer and V. May, Chem. Phys. Lett., **289**, 311 (1998).
23. B. Schmidt, P. Jungwirth, and R. B. Gerber, In M. Chergui, editor, *Femtochemistry*, page 637, World Scientific, River Edge, NJ, (1996).
24. D. T. Anderson, S. Davis, and D. J. Nesbitt, J. Chem. Phys., **107**, 1115 (1997).

25. J. M. Hutson, J. Chem. Phys., **89**, 4550 (1988).

26. A. R. Cooper and J. M. Hutson, J. Chem. Phys., **98**, 5337 (1993).

27. A. Ernesti and J. M. Hutson, J. Chem. Phys., **106**, 6288 (1997).

28. M. J. Elrod, D. W. Steyert, and R. J. Saykally, J. Chem. Phys., **94**, 58 (1991).

29. M. J. Elrod, D. W. Steyert, and R. J. Saykally, J. Chem. Phys., **95**, 3182 (1991).

30. M. J. Elrod, J. G. Loeser, and R. J. Saykally, J. Chem. Phys., **98**, 5352 (1993).

31. T. D. Klots, C. Chuang, R. S. Ruoff, T. Emilsson, and H. S. Gutowsky, J. Chem. Phys., **86**, 5315 (1987).

32. S. E. Novick, K. C. Janda, S. L. Holmgren, M. Waldman, and W. Klemperer, J. Chem. Phys., **98**, 6642 (1993).

33. P. Jungwirth, Chem. Phys. Lett., **289**, 324 (1998).

34. J. M. Hutson, J. Phys. Chem., **96**, 4237 (1992).

35. K. P. Hubert and G. Herzberg, (Van Nostrand, New York, 1979).

36. R. A. Aziz and M. J. Slaman, Mol. Phys., **58**, 679 (1986).

37. E. F. van Dishoeck, M. C. van Hemert, and A. Dalgarno, J. Chem. Phys., **77**, 3693 (1982).

38. V. Aquilanti, D. Cappelletti, V. Lorent, E. Luzzatti, and F. Pirani, J. Phys. Chem., **97**, 2063 (1993).

39. M. H. Alexander, B. Pouilly, and T. Duhoo, J. Chem. Phys., **99**, 1752 (1993).

40. P. Jungwirth and R. B. Gerber, J. Chem. Phys., **102**, 6046 (1995).

41. M. D. Feit, J. A. Fleck, Jr., and A. Steiger, J. Comp. Phys., **47**, 412 (1982).

42. D. Kosloff and R. Kosloff, J. Comp. Phys., **52**, 35 (1983).

43. A. Temperton, J. Comp. Phys., **52**, 1 (1983).

44. P. Slavicek, P. Zdanska, P. Jungwirth, R. Baumfalk, and U. Buck, J. Phys. Chem. A, submitted.

Figure Captions

Figure 1:

Ground librational wavefunctions of the HCl molecule deposited on clusters with two to six argon atoms (a)-e)). The shadowing represents the angular hydrogen probability and the wired spheres correspond to effective radii of the heavy atoms. For the sake of clarity, the radius of the hydrogen sphere is artificially expanded.

Figure 2:

a) Ground and b)-c) lowest excited librational wavefunctions of the HCl molecule deposited on clusters with twelve argon atoms. The shadowing represents the angular hydrogen probability and the wired spheres correspond to effective radii of the heavy atoms. Note the structures b) and c) corresponding to a degenerate pair of functions. For the sake of clarity, the radius of the hydrogen sphere is artificially expanded.

Figure 3:

Quantum dynamics of the radial hydrogen wavepacket motion for HCl photolysis on clusters with two to six argon atoms (a)-e)). The schematic drawing shows three possible dissociation channels: i) direct dissociation, ii) single collision, and iii) multiple collisions with the cage.

Figure 4:

Quantum dynamics of the radial hydrogen wavepacket motion for HCl photolysis on the Ar_{12} cluster initiated from the a) ground, b) first non-degenerate excited librational state.

Figure 5:

Time dependent hydrogen populations in the cluster region (as defined in the text) for systems with two to six argons.

Figure 6:

Kinetic energy distributions of hydrogen atoms produced in photolysis of HCl@Ar_n (n=2-6). For clarity, the spectra are arbitrarily vertically shifted with respect to each other.

Figure 7:

Kinetic energy distributions of hydrogen atoms produced in photolysis of HCl@Ar_{12} started from the ground (GS) or first non-degenerate excited (ES) librational states of the HCl molecule. For clarity, the spectra are arbitrarily vertically shifted with respect to each other.

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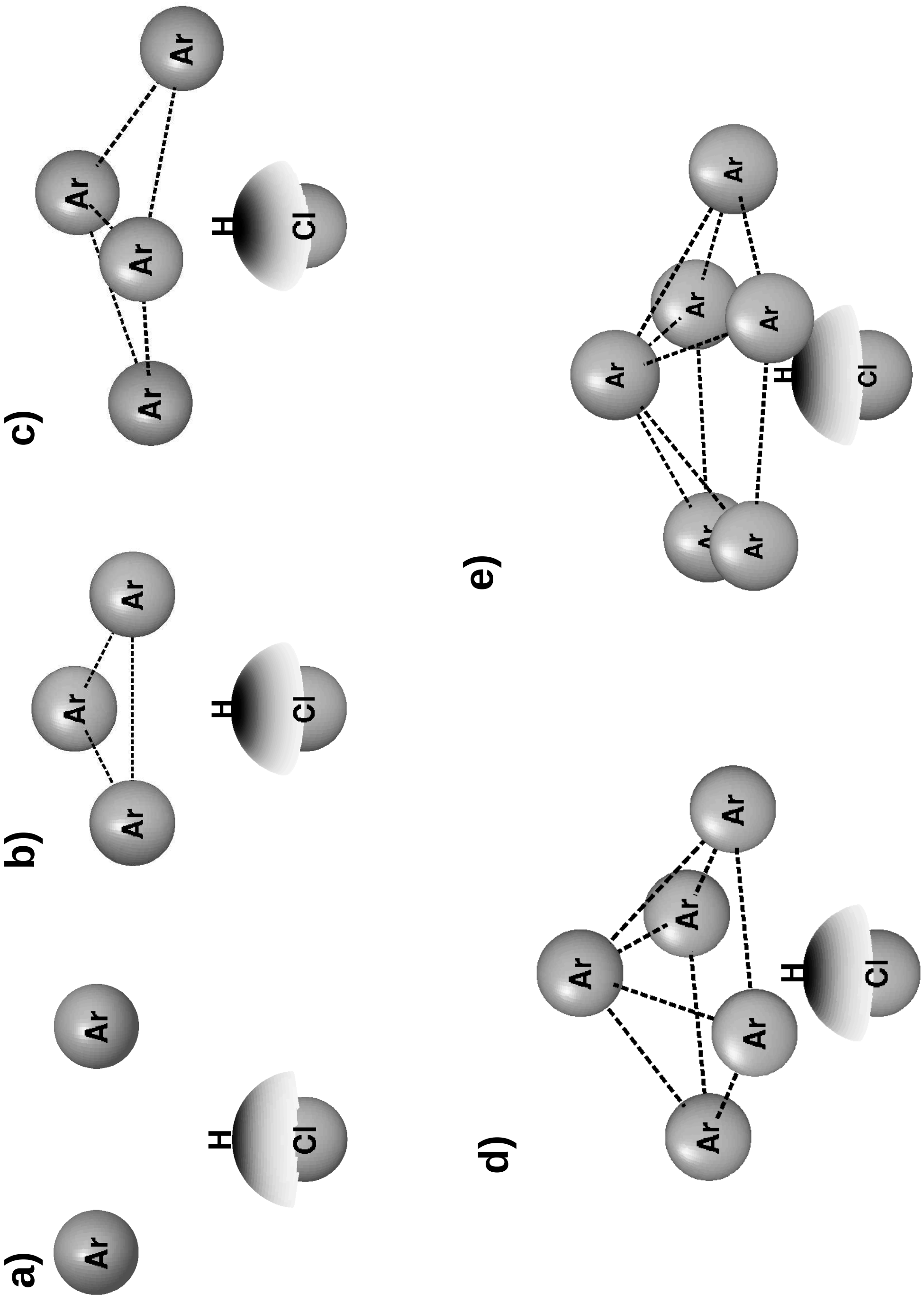

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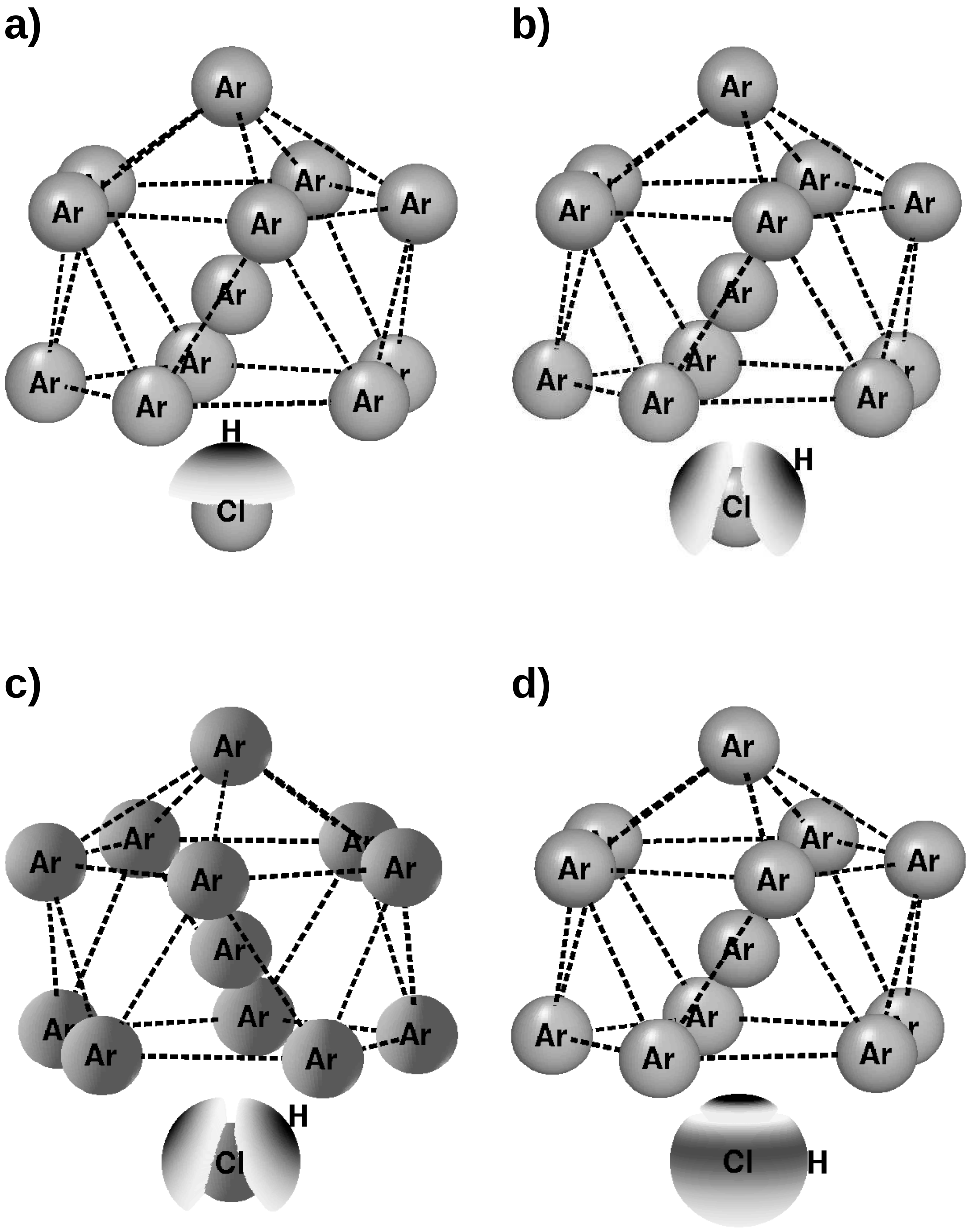

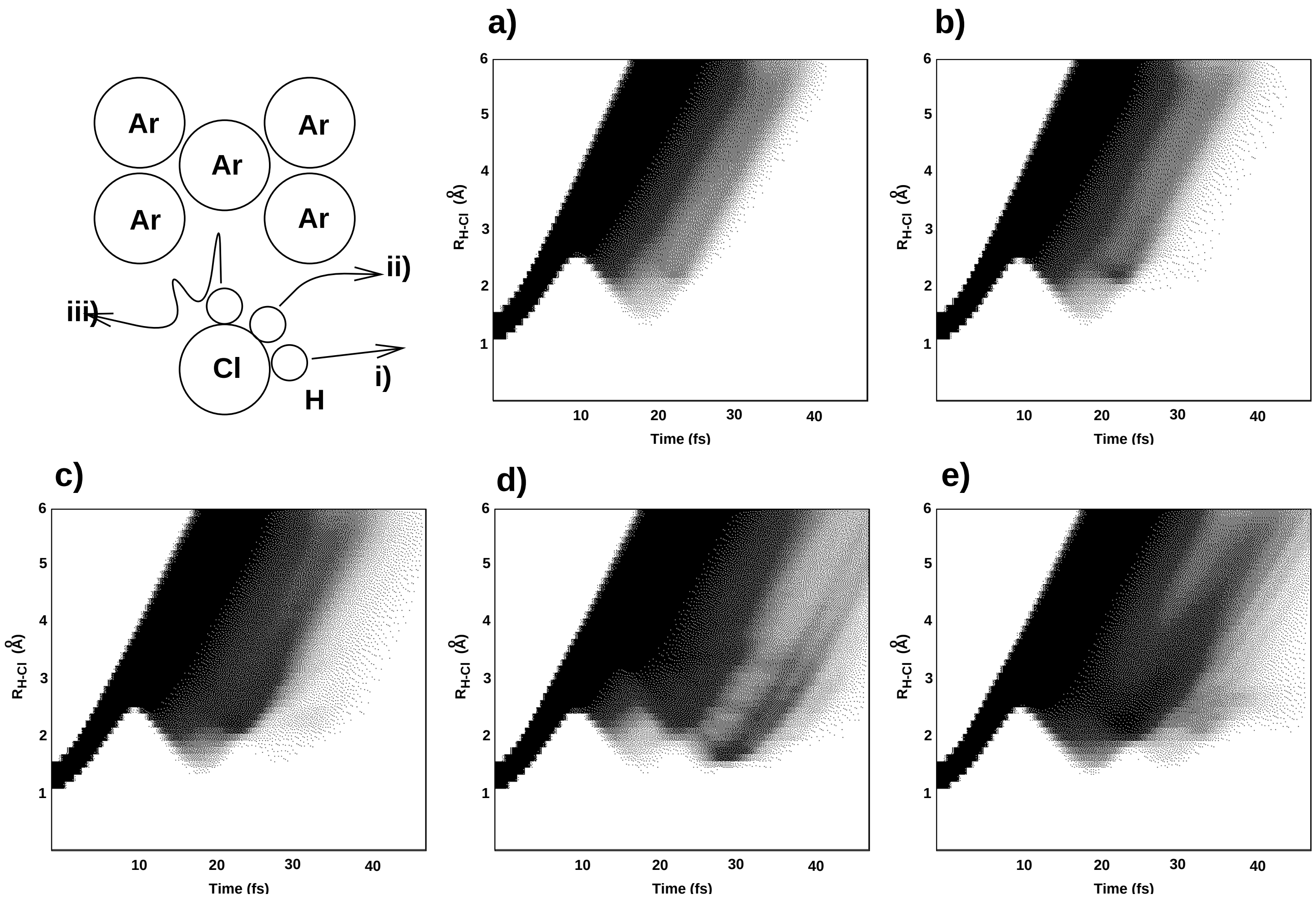

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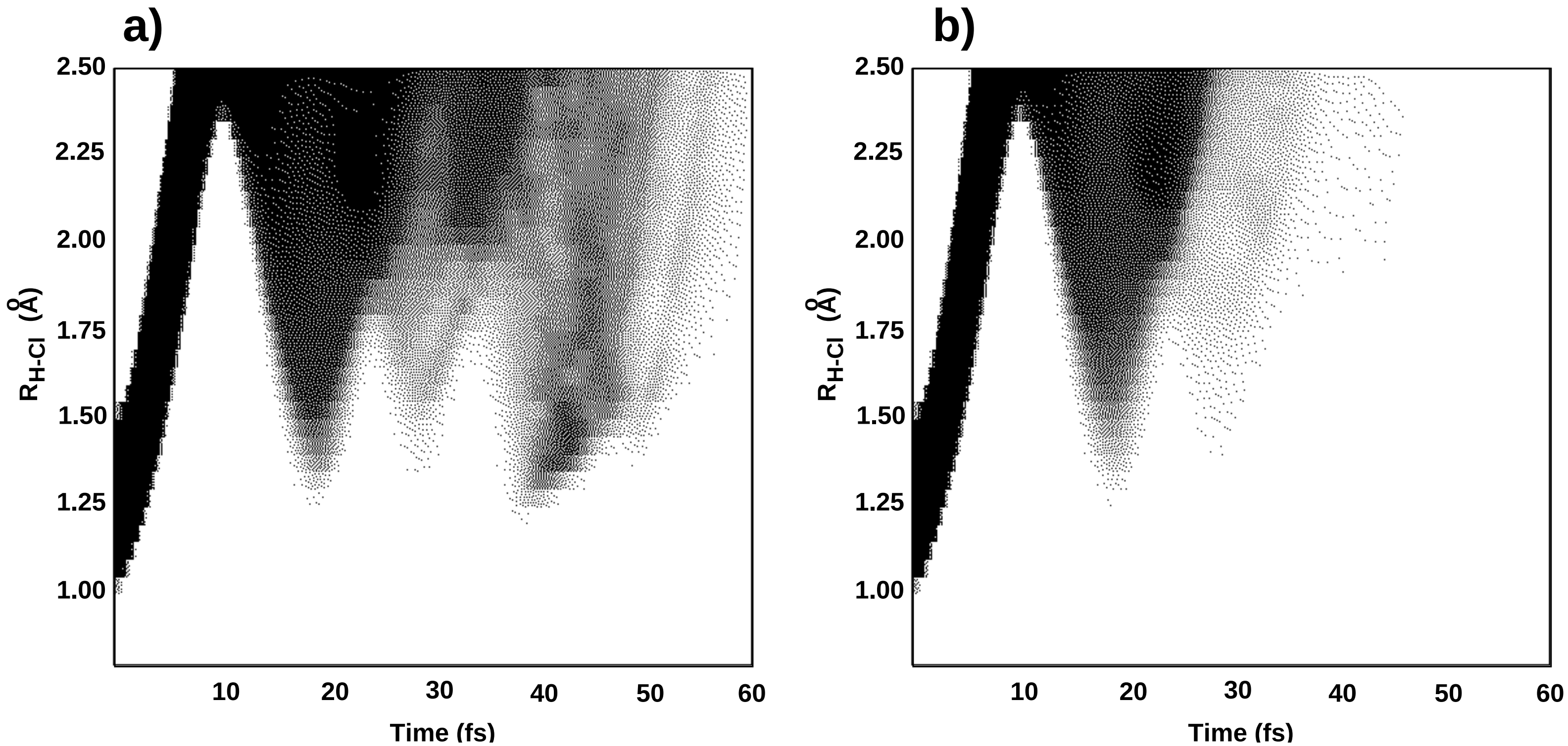

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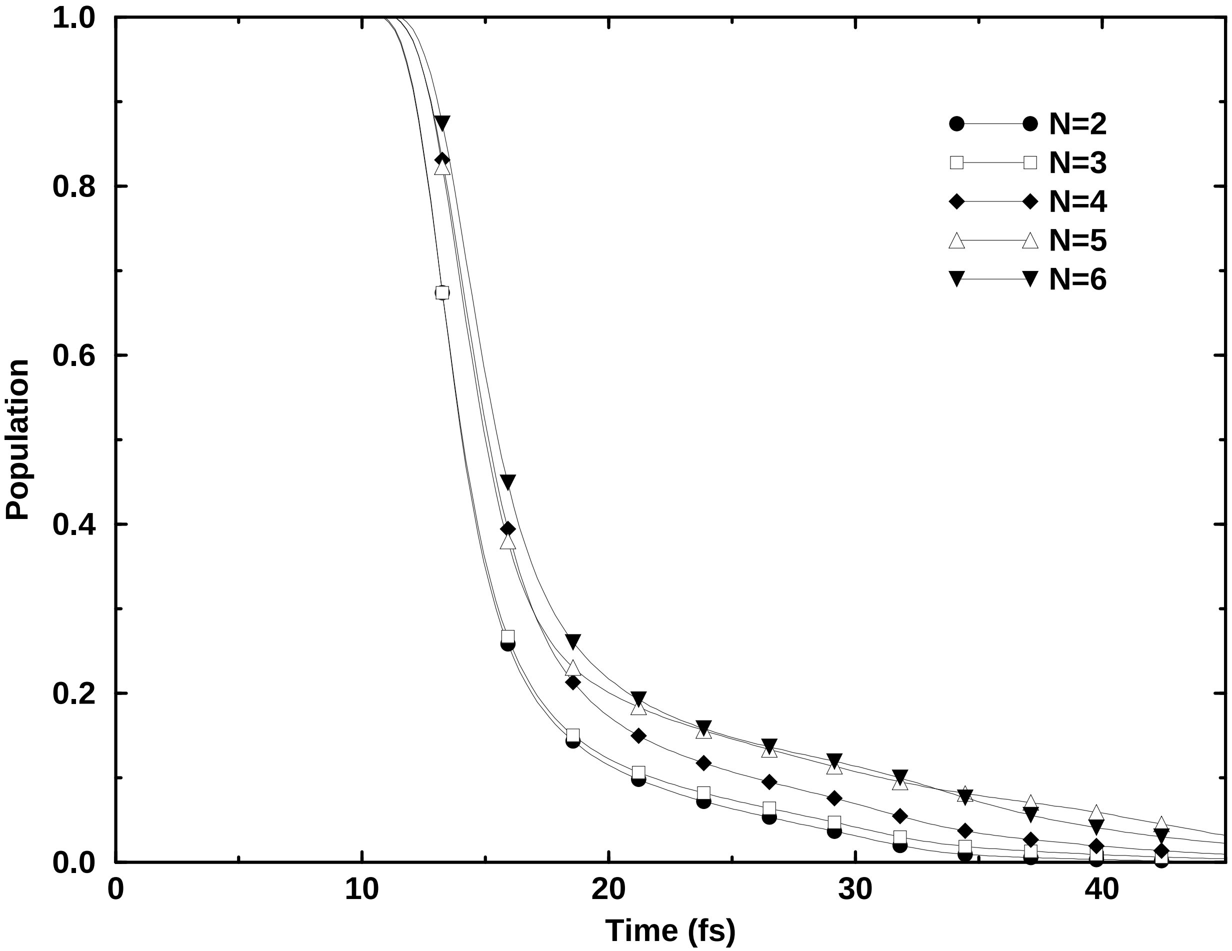

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Figure 6, Zdanska, Slavicek, Jungwirth:

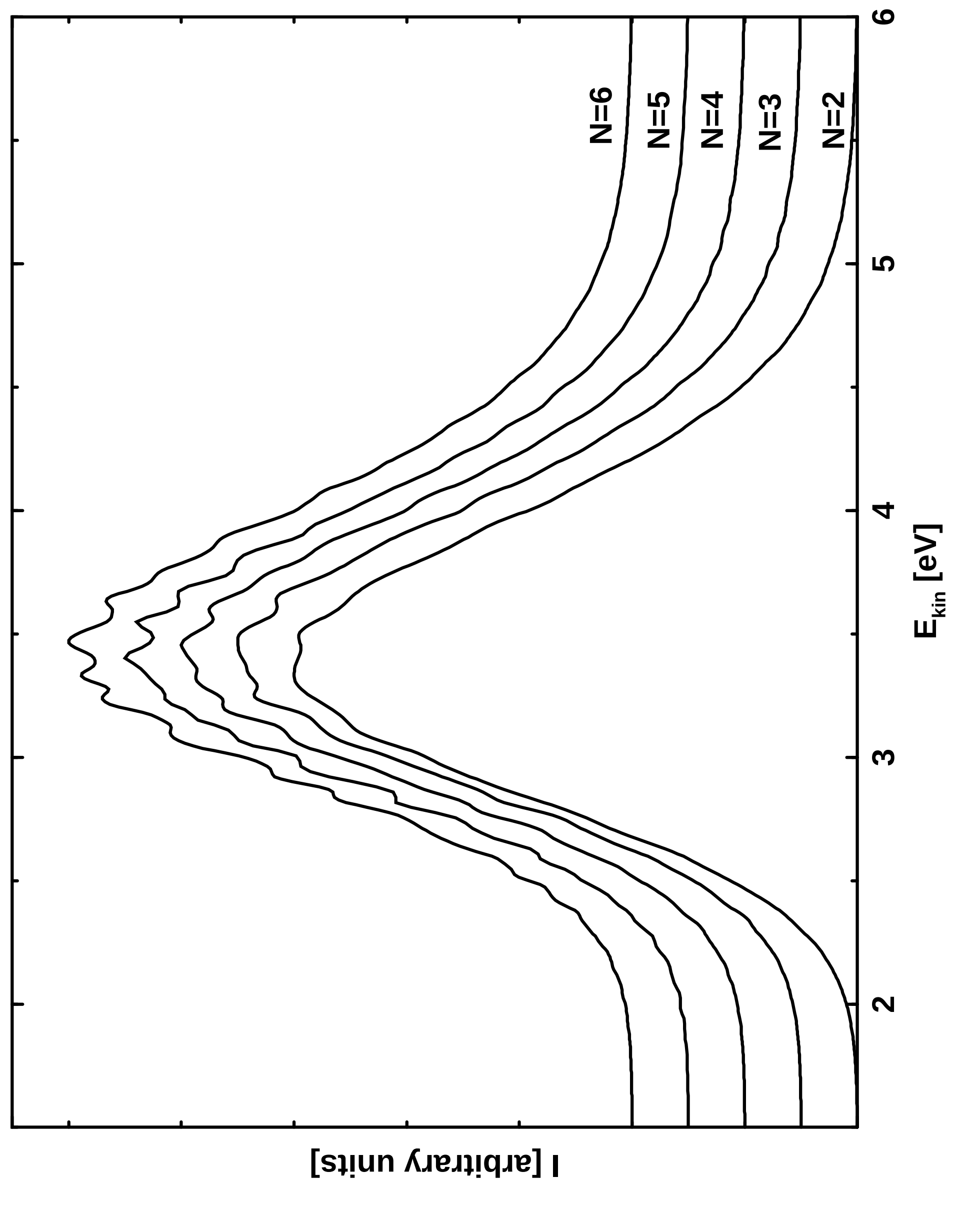

Figure 7, Zdanska, Slavicek, Jungwirth: