

QUANTUM DYNAMICS OF PHOTODISSOCIATION OF  
HYDROGEN HALIDES IN RARE GAS MATRICES.  
I. THE INITIAL STATE

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ABSTRACT

The present study focusses on the rotational motion of HCl molecules embedded in an Ar matrix. Assuming the HCl molecules to occupy substitutional sites in the fcc lattice, rotational wave functions for the vibrational and electronic ground state are obtained. Both the energetics and the spatial structure of the wave functions are investigated. While the  $J = 0$  and the  $J = 1$  state show relatively little matrix effects, all levels for  $J \geq 2$  are split. A possible control of the photodissociation dynamics by selection of rotational states of different spatial orientation is discussed.

## 1. Introduction

Photochemical processes in inert matrices have been subjected to intense experimental and theoretical investigations in recent years [1, 2, 3, 4, 5]. The most prominent effect occurring in photochemistry of condensed matter is the cage effect in which the solvent environment may cause a delay in the separation or a trapping of the photofragments, or may eventually lead to their recombination.

The present work represents a first approach to study the photodissociation of HCl in Ar (fcc) matrices. As has been discussed recently for HFAr<sub>n</sub> clusters [6], the exact knowledge of the rovibrational wavefunction of the electronic ground state prior to the excitation to a repulsive state is of great importance. This is especially so where the photodissociation dynamics strongly depends on the initial orientation of the molecule. Therefore, the highly quantum nature of the initial state of the light H-atom essentially controls the subsequent dissociation dynamics.

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## 2. Model and Potentials

The Ar lattice is modelled as a chunk of 108 atoms subject to periodic boundary conditions with a lattice constant of  $a_0 = 0.52$  nm. To simplify the computer simulations, the following assumptions are made. (1) The rare gas lattice is a perfect face-centered cubic (fcc) lattice, and lattice vibrations are ignored. These are, to a first approximation, reasonable assumptions for cryogenic matrices [1]. (2) The trapped molecules are all in monomer form which is justified for high enough mole ratios where aggregation of HCl molecules is unlikely. (3) Each of the guest molecules occupies a single substitutional site of  $O_h$  symmetry with twelve nearest neighbours along the (110)-type directions, six next-nearest neighbours along the (100)-like directions, etc. The assumption of a substitutional site can be rationalized by the comparable van der Waals radii of HCl and Ar.

To model the guest-host interaction we use pairwise additive potentials. For the electronic ground state ( $^1\Sigma$ ) we use the sophisticated Ar-HCl( $v=0$ ) atom-molecule potential by J. M. Hutson which is based on microwave and infrared spectroscopy [7]. The potential function exhibits six minima along the (100)-like directions pointing towards the next-nearest neighbors. These minima are separated from each other by twelve barriers to rotation through the (110) direction. The energetic difference between the maxima and minima is approximately  $50 \text{ cm}^{-1}$ . Between each triple of neighbouring minima/maxima there are eight saddle-like regions corresponding to the (111) directions.

## 3. Rotational Wave Functions

In the basis of the spherical harmonic functions  $Y_{Jm}(\theta, \phi)$  which diagonalize the operator of the kinetic energy the Hamiltonian matrix for a rigid rotor can be written as

$$H_{JmJ'm'} = \frac{J(J+1)}{2\mu r^2} \delta_{JJ'} \delta_{mm'} + V_{JmJ'm'} \quad (1)$$

where the potential matrix elements are defined as

$$V_{JmJ'm'} = \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi Y_{Jm}^*(\theta, \phi) V(\theta, \phi) Y_{J'm'}(\theta, \phi) \quad . \quad (2)$$

The integrations are solved numerically using a standard Gauss-Legendre quadrature scheme. Tab. 1 summarizes the resulting rotational energy levels and the symmetry of the wave functions obtained from direct diagonalization of Eq. 1. Apart from the effect of the binding energy which causes a constant energetic shift of the energy levels of  $-1796.8 \text{ cm}^{-1}$  ( $J = 0$ ) there are only small matrix effects on the four lowest levels which are almost pure  $J = 0$  and  $J = 1$  states (for a rotational constant of  $B = 10.3 \text{ cm}^{-1}$ ) with some minor admixture ( $\leq 10^{-3}$ ) of  $J = 4$  and  $J = 3, 5$  rotor states, respectively. As is well known from ligand field theory, the octahedral field causes a splitting for all levels  $J \geq 2$ . The  $J = 2$  levels is split into a twofold ( $E_g$ ) and a threefold ( $T_{2g}$ ) sublevel which are separated by  $10 \text{ cm}^{-1}$  whereas the seven  $J = 3$

Table 1: Rotational energy levels for HCl( $v=0$ )/Ar

$J$	Irrep	$E[\text{cm}^{-1}]$	orientation	$J$	Irrep	$E[\text{cm}^{-1}]$	orientation
0	$A_{1g}$	0.0	isotropic	3	$T_{1u}$	118.7	(100)
1	$T_{1u}$	20.5	(100)	3	$A_{2u}$	127.4	(111)
2	$E_g$	55.7	(100)	3	$T_{2u}$	128.0	(110)
2	$T_{2g}$	66.0	(110)				

states are split into three different sublevels also covering an energetic range of  $10 \text{ cm}^{-1}$ .

Another interesting feature is the crystallographic orientation of the probability maxima of the rotational wave functions. While the wave function of the rotational ground state is almost isotropic, the probability maxima of most of the other functions are directed along the energetically favored (100) directions. However, there are remarkable exceptions. Some of the  $J = 2$  wavefunctions ( $T_{2g}$  sublevel) are oriented along the (110) axes and one of the  $J = 3$  functions ( $A_{2u}$ ) points towards the (111) direction.

As was found previously for the case of HF/Ar, our main result is that the low barriers to rotation do not hinder the molecular rotation significantly [8]. They only cause some mixing of the free rotor states. This is most evident for the rotational ground state. While some combination of the  $J = 4$  free rotor states would fit the potential minima most snugly, the energetically lowest wave function consists mostly (0.998) of the isotropic  $J = 0$  function simply because of the much lower kinetic energy which becomes dominant over the effect of the potential barriers.

#### 4. Outlook: Rotationally Mediated Control of the Excited State Dynamics on a fs/ps Timescale

In a preliminary attempt to study the excited state dynamics we present here representative trajectories for the system HCl/Ar where the HCl molecule is in the purely repulsive first electronically excited state ( ${}^1\Pi$ ). As can be seen in Fig. 1 there are three different photochemical events: (a) For HCl initially oriented inside a narrow cone along the crystallographic (111) axis, direct cage exit ( $\approx 10 \text{ fs}$ ) through the (111) planes is possible. For other initial orientations the separation of the fragments is (b) considerably delayed or (c) does not occur inside a time window of 1 ps.

The high sensitivity of the trajectory results demonstrates the importance of the initial molecular orientation. This suggests a new possibility for the control of reactivity through selection of the different rotational states of matrix isolated molecules. Because of the different spatial orientation of the rotational wave functions it appears very likely that the quantum yield of photodissociation may be controlled within a fairly wide range. In future work this possibility of a rotationally mediated photochemistry will be investigated further by quantumdynamical simulations.

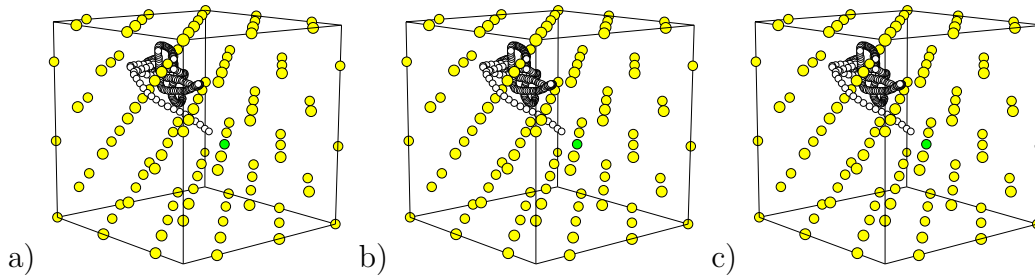


Figure 1: Classical trajectories of H-atoms for the system HCl/Ar upon electronic excitation of the HCl molecule into the  $^1\Pi$  state. a) Direct cage exit with the H-atom starting from the Cl atom (dark circle in the lower right), b) delayed cage exit after  $\approx 350$  fs, c) trapping of fragments ( $> 1$  ps).

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