

Vibrationally state-selective photoassociation by infrared sub-picosecond laser pulses: model simulations for $O + H \rightarrow OH(v)$

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10 July 1996

Abstract

The quantum dynamics of a photoassociation reaction in the electronic ground state controlled by an infrared picosecond laser pulse is investigated. The association reaction $O + H \rightarrow OH(v)$ is simulated by representative wavepackets. The OH molecule to be formed is modeled as a non-rotating Morse oscillator. It is shown that the initial free continuum state of $O + H$ can be transferred selectively into a specified vibrational bound state by interaction with an infrared laser pulse. Optimal design of the laser control field leads to high association probability with very high vibrational state selectivity.

1. Introduction

In photoassociation reactions two colliding atoms or radicals are bound by interaction with the electromagnetic laser field inducing a transition from a free continuum state to a bound state of the collision partners. Unlike the reversed process of photodissociation which has been subject to a lot of theoretical work in recent years [1], the theory of photoassociation has received little attention yet. Among the few exceptions is one study of photoassociation of Na atoms in ultracold collisions using pulsed lasers [2], which was motivated by a number of cw laser experiments on photoassociative ionization of Na_2 [3–7]. One further example is first experimental [8]

and theoretical [9] work on femtosecond photoassociation spectroscopy of Hg_2 .

This Letter presents the first investigation of the infrared (IR) photoassociation of a collision complex leading to stable products in the electronic ground state. This process of bond formation thus is a direct reversal of recently developed strategies for bond breaking by absorption of infrared photons inducing a bound–free transition in the electronic ground state [10,11]. On the contrary, the above mentioned investigations [2–9] involve absorption of a visible or ultraviolet photon transferring the collision complex into a (usually metastable) electronically excited state.

The use of IR lasers to manipulate collision pairs has already been suggested by Orel and Miller [12–14]. In their one-dimensional model simulations they have shown that chemical reactions can be enhanced mode selectively, and even the formation of a metastable intermediate in the intense IR laser

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field has been anticipated [14]. In contrast with their applications of cw IR lasers, we suggest here picosecond (ps) and/or femtosecond (fs) IR laser pulses for a definite stabilization of the collision pair, i.e. the formation of a new chemical bond.

The purpose of this study is to demonstrate the possibility of the efficient vibrational state-selective photoassociation reaction controlled by the IR ps/fs laser pulses, at least for a simplified model case, which may serve as a reference for future investigations of more realistic models or experiments. Moreover, we have already explored the effect of the probably most important parameters of the process: (i) the laser pulse amplitude and the carrier frequency, and (ii) the timing, including the laser pulse duration and the time delay between the scattering event and the beginning of the laser pulse.

In order to selectively transfer the continuum state of the scattering partners into a specific bound molecular state and to achieve high probability we propose the use of IR ps/fs laser pulses. A variety of different methods for optimal pulse shaping for coherent control can be found in the literature (for reviews, see Refs. [15,16]). Here a method is used in which the parameters of a pulse of given analytical shape are optimized [17] similarly to our previous work on excitation of very high vibrational levels and on photodissociation with ultrashort infrared laser pulses [11,18].

2. Model

The initial state of the system is a free state of $O(^3P) + H(1s)$. The relative motion of the collision partners is modeled as a Gaussian wavepacket in the distance r commonly used in the time-dependent theory of reactive scattering [19]

$$\psi(r, t=0) = \left(\frac{2}{\pi a^2}\right)^{1/4} \exp\left[ik_0 r - \left(\frac{r-r_0}{a}\right)^2\right], \quad (1)$$

representing the two atoms with average initial distance r_0 , and a (relative) momentum $\hbar k_0$. The width of the wavepacket (1) is specified by parameter a .

As the atoms come close to each other, they start to interact through the Morse potential representing

the bond to be formed. The molecular Hamiltonian is given by

$$\hat{H}_{\text{mol}}(r) = \frac{\hat{p}^2}{2m} + V(r), \quad (2)$$

where r is the distance and m is the reduced mass of 0.9482 u of the collision pair $^{16}\text{O}-^1\text{H}$. Here $V(r)$ stands for the Morse potential function for the $X^2\Pi$ electronic ground state of OH supporting 22 bound states

$$V(r) = D_e \{ \exp[-\beta(r-r_e)] - 1 \}^2 - D_e, \quad (3)$$

with equilibrium bond length $r_e = 96.36$ pm, well depth $D_e = 523.5$ kJ/mol, and Morse parameter $\beta = 22.47$ nm $^{-1}$ [20]. The interaction with a laser field which is assumed to be linearly polarized along the molecular axis is treated in the formalism of the semiclassical electric dipole approximation by the interaction Hamiltonian

$$\hat{H}_{\text{int}}(r, t) = -\hat{\mu}(r)\mathcal{E}(t), \quad (4)$$

where the molecular dipole moment operator is modelled by a Mecke function [21]

$$\hat{\mu}(r) = qr \exp(-r/r^*), \quad (5)$$

with parameters $q = 1.634 |e|$ and $r^* = 60$ pm for OH bonds in the water molecule [22]. The electric field $\mathcal{E}(t)$ of the laser is represented by a \sin^2 pulse shape of duration τ_p

$$\mathcal{E}(t) = \mathcal{E}_p \sin^2\left(\frac{\pi t}{\tau_p}\right) \cos(\omega_p t), \quad 0 \leq t \leq \tau_p, \quad (6)$$

with amplitude \mathcal{E}_p and carrier frequency ω_p .

Based on these assumptions, the wavepacket $|\psi(r, t)\rangle$ describing the dynamics of the O + H relative motion is governed by the following time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(r, t)\rangle = [\hat{H}_{\text{mol}}(r) + \hat{H}_{\text{int}}(r, t)] |\psi(r, t)\rangle. \quad (7)$$

This equation is solved numerically using a Fourier collocation scheme [23,24] for the discretization in space allowing relatively inexpensive evaluation of the kinetic energy part of Eq. (2) by means of fast Fourier transforms. The wavefunction $|\psi(r, t)\rangle$ is represented on an equidistant grid in coordinate space

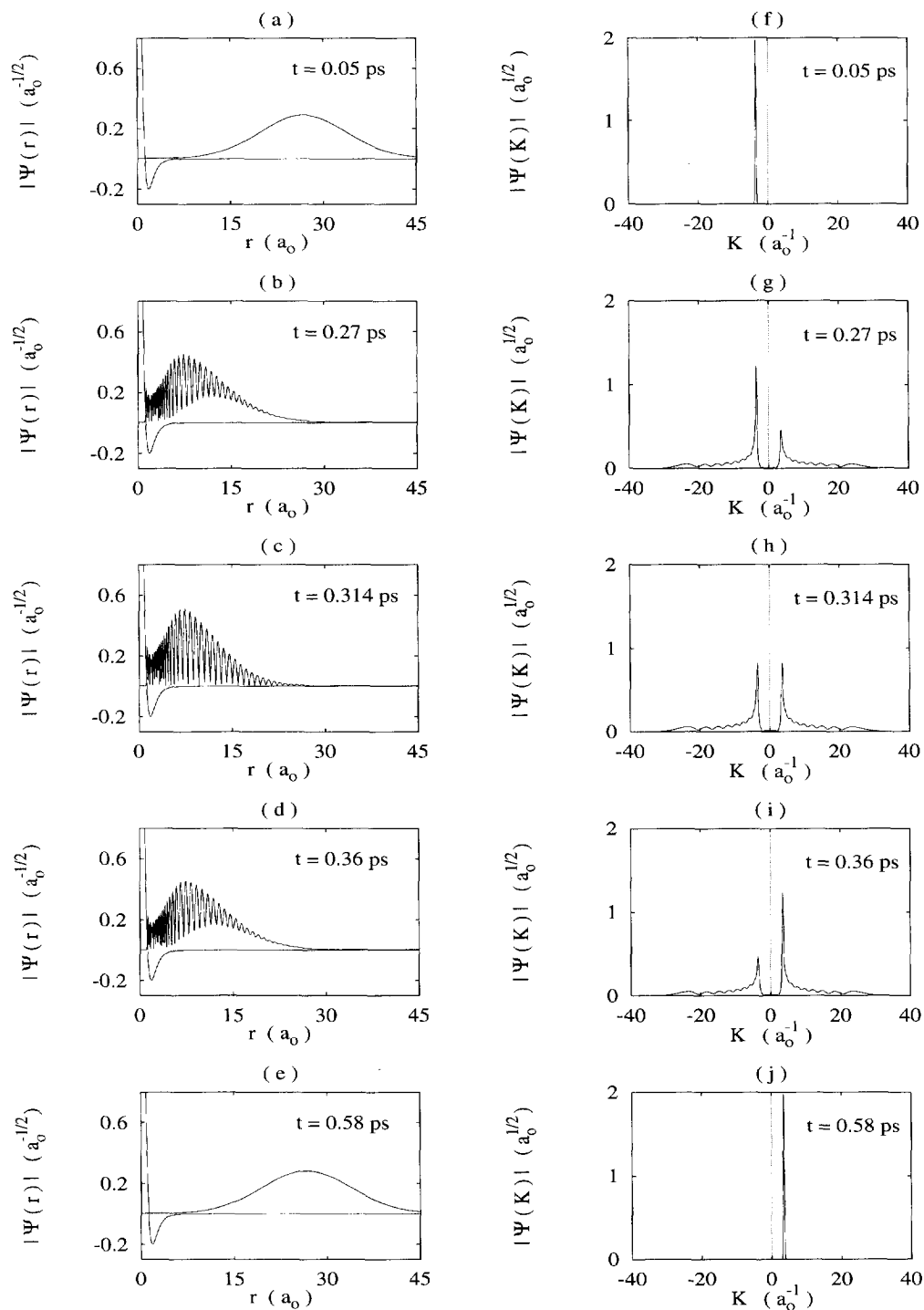


Fig. 1. Snapshots of the wavepacket dynamics of O + H elastic scattering, compare with O + H photoassociation (Fig. 3). The left column (a–e) shows the modulus of the wavefunction for various times in position space representation, the right column (f–j) shows the same in momentum space.

with 4096 grid points from 2.6 pm up to 11.64 nm. For the discretization in time we use the split-operator technique which is an $\mathcal{O}(\Delta t^3)$ approximation in the time step Δt [25,26]. Here a step width of 0.05 fs was chosen.

3. Results

First, the initial state $|E_0\rangle$ of the O + H collision has to be specified. We choose a wavenumber of $k_0 = -66.14 \text{ nm}^{-1}$ in Eq. (1) which corresponds to a relative velocity of the collision of 4.43 km/s or to a center of mass collision energy of $E_0 = 9.311 \text{ kJ/mol}$, which is in the typical order of magnitude of atomic beam experiments. Our choice for the initial width parameter a of the wavepacket is $a = 0.5212 \text{ nm}$. The center of the wavepacket in position space is chosen such that the wavepacket is just outside the interaction region, see below for the exact value.

Before investigating the photoassociation dynamics it is instructive to study the reference case of purely elastic O + H scattering, i.e. without interaction with a laser pulse. The dynamics of the collision process is illustrated in a series of snapshots of the wavepacket dynamics in position and in momentum space in Fig. 1. As the collision partners approach each other, some portion of the wavefunction is already reflected while the rest is still ingoing. This leads to interference of the ingoing and outgoing parts of the wavefunction. Outside the range of the potential energy function this gives rise to a pattern similar to a standing wave (see Fig. 1b–d), which reflects the very narrow distribution of kinetic energies due to the large value of a . This consideration of elastic scattering clearly shows the time scales which should be relevant also for the IR laser induced association. As becomes apparent from the momentum space representation the ingoing ($k < 0$) and outgoing ($k > 0$) intensities equal each other approximately at $t = 0.314 \text{ ps}$ (see Fig. 2h). Later the ingoing intensity vanishes and the scattered wavepacket is completely reversed in direction (see Fig. 2e and j), and the whole scattering event is finished at $\approx 0.58 \text{ ps}$.

Based on this we want to consider the infrared picosecond photoassociation process from the con-

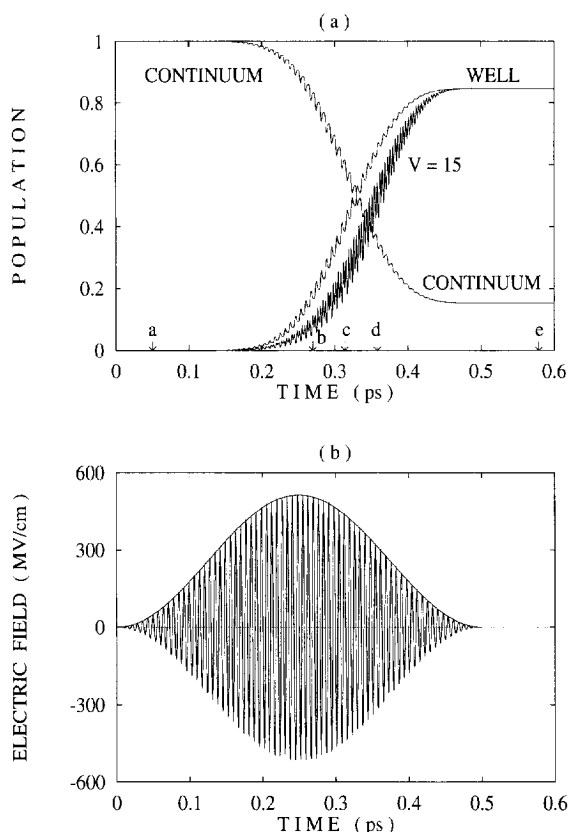


Fig. 2. Population dynamics and the optimal IR laser pulse controlling the one-photon association process of OH. (a) The curves labeled 'continuum' and 'well' give the total population of continuum states and bound states, respectively. The curve ' $v = 15$ ' gives the population of the target state $|v = 15\rangle$ only. The arrows close to the bottom indicate the times at which the snapshots of the wavepackets shown in Figs. 1 and 3 are taken. (b) Time-dependence of the electric field for the optimized IR laser pulse with $\mathcal{E}_p = 51.42 \text{ GV/m}$ and $\omega_p/(2\pi c) = 4701 \text{ cm}^{-1}$.

tinuum state $|E_0\rangle$ down to the 15th bound level chosen as a target:

$$|E_0\rangle \xrightarrow{1 \text{ photon}} |v = 15\rangle. \quad (8)$$

The collision time already gives us some guidance in the determination of the pulse length τ_p , which is determined to be 0.5 ps here. Then an optimization of the remaining parameters of the laser pulse with respect to maximizing the population of the target vibrational bound state $|v = 15\rangle$ at the end of the pulse was performed. The optimized laser pulse has an electric field amplitude of $\mathcal{E}_p = 51.42 \text{ GV/m}$ at a

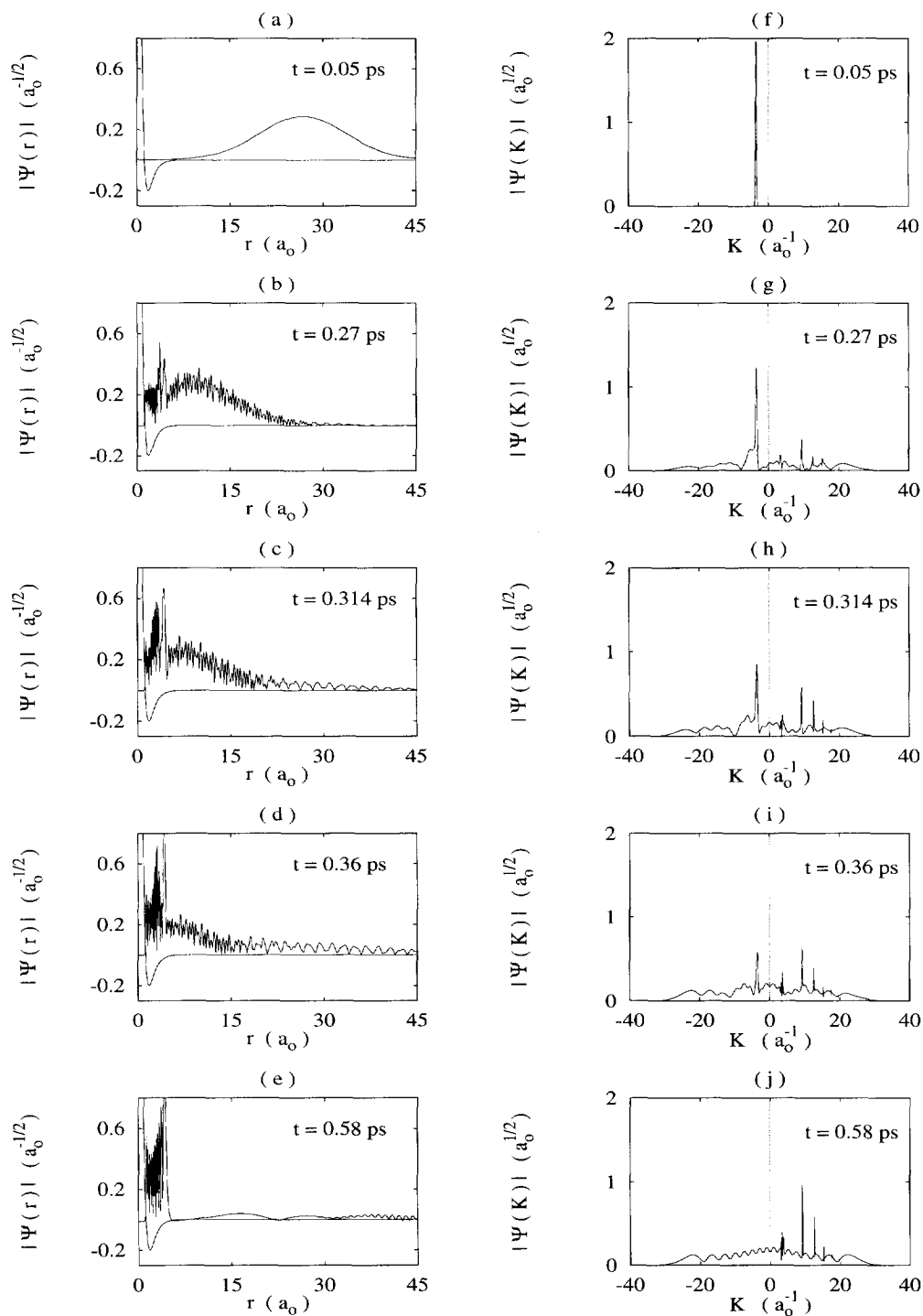


Fig. 3. Wavepacket dynamics of O + H photoassociation for the laser pulse shown in Fig. 2b, compare with the elastic scattering (Fig. 1).

photon energy of $\hbar\omega_p = 56.24$ kJ/mol, which corresponds to the laser carrier frequency $\omega_p/2\pi c = 4701$ cm^{-1} . Note that this choice corresponds to a slight detuning of the laser by $+35$ cm^{-1} , or by $+0.42$ kJ/mol with respect to the exact energy difference between the scattering state and the target bound state $|v = 15\rangle$, similar to the detunings used in simulations of the IR laser controlled state-selective dissociation on a ps/fs timescale [11]. Finally, also the time delay between the scattering event and the laser pulse has to be optimized. This is done here for a fixed beginning of the laser pulse at $t = 0$ by shifting the initial position r_0 of the center of the wavepacket in position space which results in an optimal value of $r_0 = 1.641$ nm. Alternatively, for a given value of r_0 one could determine an optimal delay of the laser pulse controlling the association reaction.

The population dynamics induced by the specified laser pulse is shown in Fig. 2a. Apart from some small amplitude oscillations, the population of the continuum state monotonically decreases down to 0.15378, i.e. the interaction with the optimal IR laser pulse transfers $P_{\text{well}} = 0.84622$ of the probability density into bound states of the potential well. Although at intermediate times ($t < 0.5$ ps) also other states (mostly $|v = 12\rangle$ which is in near-resonance) are populated, almost all of the population of the well is found in the target state $|v = 15\rangle$ at the end of the laser pulse ($P_{15} = 0.84612$). This corresponds to a vibrational selectivity of $P_{15}/P_{\text{well}} = 99.99\%$. From the comparison of the population dynamics in Fig. 2a and the time-dependence of the electric field of the laser pulse in Fig. 2b it can be seen that there is some delay between the beginning of the laser pulse ($t = 0$) and the build-up of population of bound states ($t \approx 0.2$ ps) similar to equivalent time delays for state-selective vibrational excitation and dissociation by IR laser pulses [11,18].

The wavepacket dynamics of the photoassociation process is shown in Fig. 3. In principle, there are two different effects. First, there is the dominant process of free-bound transitions by stimulated emission. The interaction with the external field effects a perturbation of the regular standing wave pattern observed for elastic scattering and leads to the build-up of population of bound states. This can be seen for the first time in the snapshots of Fig. 3b and g. The

irregular pattern of the bound state wavefunction, which is mainly a superposition of the $|v = 12\rangle$ and $|v = 15\rangle$ states, gradually transforms into the regular wavefunction of the target state $|v = 15\rangle$ at the end of the pulse (Fig. 2e and j) which at $t = 0.58$ ps is clearly separated from the continuum part in position space.

Second, the laser pulse also induces continuum-continuum transitions. As is illustrated in Fig. 3g-j, there are sharp peaks in the spectrum at positive k values. They correspond to absorption of one or more photons (here: up to four) by the part of the wavepacket which has already been reflected by the potential. Thus, the second effect of the scattering under the control of the laser pulse is considerable acceleration of the scattered particles which have not been associated.

4. Discussion

This work presents a first study of photoassociation by infrared picosecond laser pulses. As a model target for association we have considered a one-dimensional, non-rotating Morse oscillator representing the electronic ground state of the hydroxyl radical OH. For the optimal choice of the infrared picosecond laser pulse at the timing of the process we have shown that a large fraction (85%) of a scattering wave packet with $E = 9.311$ kJ/mol can be bound into the $|v = 15\rangle$ state with very high vibrational selectivity (99.99%).

Although the process of laser-controlled infrared photoassociation exhibits many analogies with the reversed process of state-selective photodissociation in the electronic ground state (see Fig. 5c and d) of Ref. [11]) there are two fundamental differences which are due to the bimolecular nature of association reactions. First of all, one has to control the timing of the onset of the laser pulse relative to the collision event. This is in contrast to photodissociation, which usually starts from a selectively prepared stationary vibrational state. Second, in photoassociation there is a strong competition among free-bound transitions leading to association and free-free transitions which give rise to acceleration of the scattered particles. While the latter ones are accessible by one-photon transitions in photoassociation, they

are only a second-order effect in photodissociation.

Of course, a more realistic approach would have to include the effect of angular momentum and of molecular rotation. For the case of photodissociation it has been shown that the main feature of the one-dimensional picture, specifically the vibrational selectivity, are preserved in a full-dimensional treatment of the problem [10]. Another class of effects which have been neglected here involves the electronic degrees of freedom, see the study of the dynamics of photodissociation of OH in several coupled electronic states [27]. A complete theoretical treatment of photoassociation would have to include non-adiabatic effects connected with the orbital re-orientation of the O(³P) atom, see for example a study of the non-adiabatic dynamics of Cl(²P) atoms in solid Ar [28].

An interesting question is the generalization of the $|E_0\rangle \rightarrow |v=15\rangle$ photoassociation investigated here to other free or bound states. As will be shown in our future work, higher vibrational levels (except for the very highest $v=21$) can be populated with comparable efficiency. However, the possibilities to populate much lower vibrational states directly from a continuum state, or to populate a given vibrational level from higher continuum states, are limited. This is caused by the continuum-bound dipole coupling function $\langle E|\mu|v\rangle$ which decreases rapidly both with decreasing vibrational quantum number v and with increasing energy E of the continuum state [18]. One way to circumvent this problem without having to go to higher laser intensities is to use a sequence of laser pulses. Sequences of one-photon and/or multiphoton transitions realized by partially overlapping laser pulses have already shown to be an effective tool in population of highly excited vibrational state [10,11,18], and they may also be useful in coherent state-selective control of photoassociation.

Acknowledgement

Financial support by the Deutsche Forschungsge-

meinschaft (DFG) through grant Ma 515/14-1 is gratefully acknowledged.

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