Detailed model study of dissipative quantum dynamics of $K_2$ attached to helium nanodroplets

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Abstract. We thoroughly investigate vibrational quantum dynamics of dimers attached to He droplets, motivated by recent measurements with $K_2$ (Claas et al 2006 J. Phys. B: At. Mol. Opt. Phys. 39 S1151). For those femtosecond pump–probe experiments, the crucial observed features are not reproduced by gas-phase calculations, but agreement is found using a description based on dissipative quantum dynamics, as briefly shown in the work by Schlesinger et al (2010 Chem. Phys. Lett. 490 245–8). Here we present a detailed study of the influence of possible effects induced by the droplet. The helium droplet causes electronic decoherence, shifts of potential surfaces and relaxation of wave packets in attached dimers. Moreover, a realistic description of (stochastic) desorption of dimers off the droplet needs to be taken into account. Step by step, we include and study the importance of these effects in our full quantum calculation of the effective dimer dynamics. This approach allows us to reproduce and explain all major experimental findings. We find that desorption is fast and occurs within 2–10 ps after electronic excitation. A further finding is that slow vibrational motion in the ground state can be considered frictionless.

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1. Introduction

Helium nanodroplet isolation (HENDI) spectroscopy allows us to study atoms, molecules and clusters embedded in an ideal cryogenic environment [3]. Ultracold helium droplets (0.38 K) provide a gentle, since weakly disturbing, host for embedded species, which can be studied with high-resolution spectroscopy [4]. However, spectra of immersed species are slightly broadened and shifted away from their gas-phase value due to their interaction with the surrounding He droplet. Inhomogeneous broadening in pure rotational spectra is ascribed to the motion of the purity inside the droplet [5, 6] or to coupling to collective degrees of freedom of the droplet [7].

The overall spectral features, which are unseen in gas-phase measurements, have been used to study the weak interaction between dopant and helium droplet [5, 8–12]. Attached species allow us to probe the peculiar properties of the superfluid He droplet itself [13]. Further insight into the interaction and the quantum properties of the droplet can be gained from recent time-resolved studies [1, 2, 14, 15].

Helium nanodroplets, typically consisting of several thousands of $^4$He atoms, are ideally suited for studying relaxation (cooling) of embedded species [16–20]. Whether dissipation plays a role depends on the involved energy scales, the coupling strengths or typical time scales in the system and ‘bath’ [21, 22]. The group of Miller has studied relaxation of hydrogen fluoride (HF) inside He droplets [23]. They have reported on ineffective vibrational relaxation due to a mismatch in energy scales. However, rotational relaxation in the immersed HF system is fast and appears as Lorentzian line broadening in the rotational transition spectrum. (See also [7] and references therein.)

Alkali metal atoms and molecules are known to reside in bubble-like structures on the surface of He droplets [24–26]. Attached $\text{Rb}_2$ dimers in the triplet state reveal the presence of vibrational relaxation on the measurement timescale [15, 27]. For lithium dimers interacting with a He environment, vibrational relaxation has been investigated by means of Monte Carlo calculations [28], including a few He atoms. The corresponding relaxation rates depend on whether the dimer is orientated in-plane or out-of-plane with respect to the He surface [29].

Femtosecond pump–probe techniques are established tools for analyzing the ultrafast vibrational motion in molecular systems [30–32]. A first laser pulse excites a coherent wave packet (WP), which is allowed to freely evolve on the respective energy surface. The WP is
probed by a time-delayed pulse. Since the early studies by the Zewail group [33, 34], vibrational WPs in various diatomic systems have been studied, such as Na$_2$ [35] or K$_2$ [36–38]. When molecules are located in a solid rare-gas matrix [39, 40], a suppression of revival structures in the pump–probe signal indicates a loss of vibrational coherence. Meier [41] has thoroughly investigated such decoherence in molecular systems placed in a rare-gas environment, motivated by seminal experiments of the Zewail group [42]. For experiments at room temperature with a significant thermal occupation of rotational states, unavoidable coupling between internal vibrational and rotational degrees of freedom may lead to sufficient decoherence to suppress (fractional) revivals [43]. Experiments with Rb$_2$ dimers on He droplets reveal an ongoing decay of the pump–probe ion yield [14]. The decay has been ascribed to damping and accompanying decoherence of vibrational WPs [15]. In this work, we investigate potassium dimers on He droplets, studied experimentally with the pump–probe technique [1]. A brief account of a theoretical description based on dissipative quantum dynamics was given in [2]. Experimental spectra show significant deviations from corresponding gas-phase calculations for the unperturbed dimer.

A fully quantum treatment in terms of dimer and droplet degrees of freedom is desirable in order to shed light on the intricate coupled dynamics of molecules and droplets. As a first step, in this paper, we investigate in detail how the helium influence may be described effectively. First, we see that the helium environment destroys electronic coherence, which is imprinted by the exciting laser pulse. As possible causes for electronic decoherence, we consider a distribution of shifts of electronic surfaces. Electronic decoherence alone cannot account for the decay of the signal at certain excitation wavelengths. Therefore, in a following step, we include a general damping of vibrational WPs on each electronic surface. The effective dynamics is described by means of a quantum optical (Markovian) master equation, reflecting a phenomenological approach. In a next step, a microscopic derivation of such a master equation will be sought, which would also clarify the significance of the usual approximations being made (Born and Markov). This, however, is clearly beyond the scope of the present paper, which shows that already on a phenomenological level all major experimental findings can be reproduced.

In addition to the aforementioned mechanisms, it is important to properly take into account the desorption of dimers from the droplet. No general rule can be given when attached atoms or molecules leave the droplet. It is known that lighter alkali metal atoms leave the droplet upon electronic excitation [44] or form a bound exciplex [45]. The exciplex tends to desorb off the droplet surface during the formation process or several picoseconds thereafter [46]. On the other hand, desorption of Rb atoms may be completely inhibited upon electronic excitation in a certain laser wavelength range [47]. Recent measurements indicate that K$_2$ molecules desorb several picoseconds after laser excitation [1]. Indeed, (stochastic) desorption of dimers is a crucial ingredient to explain spectral features with a theoretical model [2].

We report here on a more realistic description of desorption—we use a model that only allows electronically excited molecules to leave the droplet. We thus extend our previous, state-independent desorption scheme [2]. Together with dissipation and shifts of potential energy surfaces, one can explain experimental findings over the full laser excitation range reported in [1].

This paper is organized as follows. In section 2, we review the calculation of the pump–probe signal for free dimers. In section 3, the influence of the helium environment is considered in a phenomenological way. In section 3.3, we explain how we treat desorption of dimers. Finally, for even better agreement with experiment, we consider undamped motion in the
Figure 1. Excitation schemes in the potassium dimer for two distinct laser wavelengths $\lambda = 833$ nm (scheme I) and $\lambda = 800$ nm (scheme II). While the first scheme exclusively maps the WP in the $A^1\Sigma^+_u$ state, the second scheme allows us to observe the WP in the ground state $X^1\Sigma^+_g$.

Electronic ground state. A thorough comparison between theoretical and experimental findings is given at every step in the model. Section 4 is devoted to the conclusions.

2. Pump–probe signal

A first ‘pump’ laser pulse creates a vibrational WP $|\psi_i\rangle$ in some electronic state $|i\rangle$. The excited WP oscillates in a region between the classical inner and outer turning points of that surface. It may periodically enter and leave a transition region, where a resonance condition with higher-lying states is met and the potential energy difference matches the second, ‘probe’ pulse energy. This region defines the so-called Franck–Condon (FC) window. The time-delayed probe pulse leads to a significant number of ions only when the WP is located in the FC window. By varying the time delay $\tau$ between the pump and probe pulses, one obtains an oscillatory ion yield. A typical excitation scheme is depicted in figure 1(a), where one probes the dynamics of the WP on the $A^1\Sigma^+_u$ surface.

WPs may be excited in several involved electronic surfaces of the dimer. More specifically, the pump pulse prepares the dimer in a superposition of electronic states. When the pump pulse has passed (at $t \simeq t_{\text{pump}}$), the full state vector $|\Psi\rangle$ takes the form

$$|\Psi(t_{\text{pump}})\rangle = \sum_i |\psi_i\rangle|i\rangle. \quad (1)$$

Here, $\psi_i$ denotes the WP on a specific electronic state $i$ and

$$p_i = \langle \psi_i | \psi_i \rangle \quad (2)$$

is the probability that the electronic state $i$ is excited.
For the pump–probe signal, we fully numerically solve the time-dependent Schrödinger equation

\[
\frac{i\hbar}{\partial t} \begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \\ \psi_3(E) \end{pmatrix} = \begin{pmatrix} H_0 & J_{01} & 0 & 0 \\ J_{10} & H_1 & J_{12} & 0 \\ 0 & J_{21} & H_2 & J_{23} \\ 0 & 0 & J_{32} & H_3(E) \end{pmatrix} \begin{pmatrix} \psi_0 \\ \psi_1 \\ \psi_2 \\ \psi_3(E) \end{pmatrix},
\]

for the full state vector \(|\Psi\rangle\) (see also [36, 48]). In the matrix equation, the diagonal elements denote the molecular Hamiltonian \(H_{\text{mol}} = \sum_i H_i = T + \sum_i V_i\), which involves kinetic energy \(T = \frac{P^2}{2\mu}\) (reduced mass \(\mu\)) and adiabatic potentials \(V_i\). The employed electronic states \(i = 0, 1, \ldots\) correspond to \(X^1\Sigma^+_g, A^1\Sigma^+_u, \ldots\) shown in figure 1. In the final ionic state, the energy \(E\) of the ejected electron is included in the diagonal entry of the Hamiltonian \(H_{3,E}\), such that \(V_{\text{F3 Final}} = V_3 + E\). The coupling to the laser field is described by the matrix elements \(J_{ij} = -\vec{\mu}_{ij} \cdot \vec{E}(t)\), where \(\vec{\mu}_{ij}\) denotes the transition dipole moment. Both pump and probe pulses have the form \(\tilde{E}_{\text{pump/probe}}(t) = \tilde{\epsilon}_0 e^{i(\omega_0 t + \xi)}\) and \(\omega_0\) is the respective laser frequency. Moreover, \(\tilde{\epsilon}_0\) is the polarization and \(\xi(t)\) the shape function of the field, which is assumed to be Gaussian. For the field parameters we use a full-width at half-maximum of the laser pulse of 110 fs and an intensity of \(I = 1.2\) GW cm\(^{-2}\), which leads to the best agreement with experiment over the entire frequency range. Note that in [1] a value of \(I = 0.5\) GW cm\(^{-2}\) is estimated with, however, a large margin of uncertainty [59]. In any case, according to [36], both values are located in the moderate power regime. The ionic state \(|\psi_3(E)\rangle\) also depends on the energy \(E\) of the ejected electron. We use discretization of the (electronic) continuum, a technique successfully employed earlier [48]. One determines the final state probability \(|\psi_3(E_k)\rangle^2\) after both pulses have passed for distinct electronic energies \(E_k\). The pump–probe signal is proportional to the sum over different electronic contributions,

\[
S(\tau) = \lim_{t \to \infty} \sum_{E_k} |\psi_3(\tau, E_k)|^2.
\]

In the limit \(t \to \infty\) (upon complete decay of the second pulse), it only depends on the delay \(\tau\) between the pulses. For the propagation of the wave function, we use the split-operator method [49].

The ion signal is composed of beat frequencies \(\omega_{vv'} \equiv (E_v - E_{v'})/\hbar\) between all pairs of energy levels that contribute to the WP [15]. The laser frequency determines the central level \(\bar{v}\) in the superposition, i.e. the level with the largest vibrational occupation probability (vertical transition). The most prominent oscillation originates from the energy spacing between the central and neighboring vibrational levels \(\bar{v}\) and \(\bar{v} \pm 1\). This oscillation has the frequency

\[
\omega_i = \omega_{\bar{v}, \bar{v}+1}
\]

and is characteristic of the electronic surface \(i\). In an anharmonic potential, the level spacing and therefore also \(\omega_i\) decrease as \(\bar{v}\) increases. Higher-order frequency components \(\omega_{\bar{v}, \bar{v}+\Delta v}\) with \(\Delta v > 1\) are visible in the Fourier transform of the signal.

The laser wavelength \(\lambda\) determines which WPs \(\psi_i\) can be mapped to the final state. In the one-color pump–probe setup, we consider two different excitation schemes.

For 820 nm \(\lesssim \lambda \lesssim 840\) nm (scheme I), one exclusively follows the vibrational dynamics in the excited state \(A^1\Sigma^+_u\). The WP in that state can be probed at the outer turning point (see
For 800 \( \lesssim \lambda \lesssim 820 \) nm (scheme II), transitions preferably take place at the inner turning point of the excited WP. The WP in the electronic ground state \( X^1\Sigma^+_g \) is excited through resonant impulsive stimulated Raman scattering. It can be probed through a three-photon process, see figure 1. On the other hand, simultaneous and coherent contributions from WPs in electronic excited states lead to constructive or destructive interferences and thus to an unstructured ion yield [38]. We use sliding window Fourier transforms \( \mathcal{F}(\omega, \tau) \) to follow the evolution of respective beat frequency components as a function of delay time [50, 51]. Figure 3(a) shows a window transform (spectrogram) for excitation at \( \lambda = 800 \) nm. A frequency component \( \omega_A \approx 63 \text{ cm}^{-1} \) can be ascribed to the WP in the state \( A^1\Pi^+_u \). Moreover, a higher-order frequency component at \( \approx 2\omega_A \) is visible as is a significant contribution at \( \omega \approx 85 \text{ cm}^{-1} \) after about 15 ps that can be traced back to originate from the \( 2^1\Pi_g \) surface. A contribution from the ground state and the resulting frequency component \( \omega_X \), however, is missing. In agreement with earlier findings [36, 38], the mapping of the ground-state WP is not possible at low-to-intermediate intensities in the gas phase. This is because, as explained below, the contributions from different potential energy surfaces interfere destructively. In contrast, for dimers attached to He droplets, the contribution from the state \( A^1\Sigma^+_u \) is suppressed after about 8 ps, while on the other hand, the vibrational ground-state WP is clearly resolved, see figure 3(b).

Qualitatively, the difference between figure 3(a) (gas phase) and figure 3(b) (experiment) can be explained by the loss of electronic coherence alone: in figure 4, we construct an artificial signal from the incoherent sum of contributions. The full coherent wave vector after decay of the pump pulse at \( t \equiv t_{\text{pump}} \), equation (1), serves as a starting point. In order to determine the contribution of a single WP \( \psi_i \), we project the fully coherent wave vector according to \( \tilde{\Psi}(t_{\text{pump}}) = P_i \Psi(t_{\text{pump}}) \) with the projector \( P_i = |i\rangle \langle i| \) on one of the electronic states. The electronic occupation \( p_i \) is not altered and the usual probe scheme is employed after projection.
Figure 3. Spectra $\mathcal{F}(\omega, \tau)$ in the time–frequency domain at $\lambda = 800$ nm. (a) Numerical gas-phase calculation, where electronic interferences lead to a spectrum that is difficult to interpret. (b) Experimental result (from [1]). Electronic interferences are absent, allowing for a clear identification of the structures of the spectrum.

Figure 4. The spectrogram $\mathcal{F}^i(\omega, \tau)$, obtained on projecting the created full wave function $\Psi(t)$ on (a) the electronic ground state ($i = 0$) and (b) the first excited state ($i = 1$). (c) In the incoherent sum, interferences are excluded. In particular, the ground-state component is clearly resolved.

The resulting spectrogram $\mathcal{F}^{inc}(\omega, \tau)$ after projection on the states $A^1 \Sigma_u^+$ and $X^1 \Sigma_g^+$, respectively, is shown in figures 4(a) and (b). The incoherent sum of contributions is given by

$$\mathcal{F}^{inc}(\omega, \tau) = \sum_i \mathcal{F}^i(\omega, \tau).$$

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Contrary to the coherent signal, figure 3(a), in equation (6) interferences are removed by hand and contributions from ground- and excited-state WPs are clearly visible. Obviously, the incoherent sum (figure 4(c)) already reproduces important features of the experimental data. In the experiment (figure 3(b)), however, the component $\omega_A$ fades out at later delay times, while the component $\omega_X$ becomes dominant. Therefore, a model based on pure loss of electronic coherence alone cannot explain the measured spectrum. One has to consider the additional influences of the He environment on the dimer dynamics.

3. Helium influence and results

In a phenomenological approach, we take into account three possible effects.

(i) A He-induced energetic shift of electronic potential energy surfaces, with possibly small fluctuations.

(ii) Damping of vibrational WPs. This effect is treated fully quantum mechanically within the master equation approach. The WP $\psi_i$ dissipates energy with a certain damping rate $\gamma_i$. This rate is here seen as a fit parameter and is adjusted to experimental observations.

(iii) Desorption of dimers off the droplet. After desorption, the influence of the helium droplet (shift/damping) vanishes.

A description based on damping of vibrational WPs has been applied to HENDI studies with spin triplet Rb$_2$ dimers [15]. There, slow vibrational decoherence (as a consequence of very weak dissipation) is most relevant for the decay of the revival amplitude. In particular, as witnessed by the ongoing decay, desorption of dimers seems to be inhibited.

In the following, step by step, we include shift, damping and finally desorption in the calculation of pump–probe spectra. It is found that all model ‘ingredients’ (i)–(iii) are crucial to find agreement with obtained experimental spectra.

3.1. Electronic shifts

The He environment may lead to shifts of electronic surfaces in attached dimers. Such shifts are common for alkali atoms and molecules on He droplets [27]. Spectra from attached species are shifted relative to what one expects from gas-phase potential energy curves [52–56]. For certain weakly coupled species, spectra are only shifted by a few wave numbers [27]. Denoting the shift of surface $i$ with $\Delta_i$, the full state vector is propagated according to

$$|\Psi(t)\rangle = -\frac{i}{\hbar} H|\Psi(t)\rangle + \frac{i}{\hbar} \sum_i \Delta_i |\psi_i\rangle.$$  

(7)

Both surfaces $A^1 \Sigma_u^+$ and $2^1 \Pi_g$ may be affected. Only relative shifts are relevant for the signal, such that we cannot differentiate between a shift of the electronic ground and first excited states. Also, a shift of the ionic surface would change the energy distribution of the ejected electrons, but not the overall calculated ion yield. This is because we sum over all electronic energies in equation (4). We find that even large, but fixed shifts of up to $\pm 100 \text{ cm}^{-1}$ have a very small influence and resemble the gas-phase calculation.

However, it is reasonable to assume that the shifts $\Delta_i$ fluctuate for the following reason: the number of He atoms of a droplet is not fixed but varies according to a log-normal
distribution [57]. Consequently, we have to average over a distribution of shifts $\Delta_i$ [58]. Also, for the considered laser intensities, electronic surfaces are slightly Stark-shifted. Depending on their position in the laser beam, dimers are exposed to a distribution of laser intensities [59]. The beam width leads to a distribution of Stark shifts, which in turn has to be treated as a random distribution of electronic shifts $\Delta_i$.

Considering fluctuating potential energies, equation (7) represents only a single realization $|\psi_j(t)\rangle$ with shifts $\Delta_i(j)$ in the ensemble. The pump–probe signal is proportional to the ensemble average

$$\langle S(\tau) \rangle = \frac{1}{N} \sum_j \left[ \lim_{t \to \infty} \sum_{E_k} |\psi_{j,3}(\tau, E_k)|^2 \right],$$

where $N$ realizations have been taken into account. In this expression, the final state $|\psi_{j,3}\rangle$ is obtained from propagation of the realization $|\psi_j(t)\rangle$, in which $\Delta_i(j)$ is chosen randomly. Through the ensemble average in equation (8), one obtains an incoherent mixture of electronic contributions in the final state. The spectrogram of $\langle S(\tau) \rangle$ nearly perfectly resembles the incoherent sum of contributions, see equation (6) and figure 4(c). It does not contain any electronic coherence, such that the frequency components $\omega_i$ are clearly resolved. For full decoherence (figure 4(c)), random shifts in the range of $\pm 5 \text{cm}^{-1}$ around the average shifts $\overline{\Delta_1} = 0 \text{cm}^{-1}$ and $\overline{\Delta_2} = -50 \text{cm}^{-1}$ are sufficient. Note that this decoherence is due to the inhomogeneous size distribution and not due to entanglement between the system and the environment [60, 61].

To conclude, randomly distributed energy shifts can explain the visibility of the ground-state component $\omega_X$. However, this effect lacks an explanation for the decay of the frequency component $\omega_A$ of the excited state, which is observed in the HENDI experiment. Therefore, we next consider vibrational damping.

3.2. Damped vibrational wave packets (WPs)

Dissipation can be treated fully quantum mechanically by using approximate master equations for the density operator of the (reduced) system. The overall dissipation of an excited WP originates in our case from the interaction of vibrational degrees of freedom of the molecule with collective degrees of freedom of the helium droplet. Note that in recent studies [29] vibrational relaxation rates for alkali dimers on $^4$He clusters are estimated from full quantum Monte Carlo calculations for a few He atoms. These rates turn out to be roughly of the same order of magnitude as our phenomenologically chosen damping rates below.

In our approach, the density $\rho$ of the damped WP in an electronic state $|i\rangle$ evolves according to the master equation

$$\dot{\rho} = -\frac{i}{\hbar}[H_i, \rho] + \gamma \left( a \rho a^\dagger - \frac{1}{2} a^\dagger a \rho - \frac{1}{2} \rho a^\dagger a \right),$$

which is of the Lindblad form [62]. It describes friction for near-harmonic systems at effectively zero temperature in the rotating wave approximation (see, e.g., [63, 64]). The first term in equation (9) contains the molecular Hamiltonian $H_i$ of a specific electronic state $|i\rangle$ and determines the unitary evolution of the WP $|\psi_i\rangle$. Relaxation of the vibrational WP is achieved through the second, irreversible contribution. Any initial state approaches the ground
state on a timescale $\gamma^{-1}$, i.e. $\gamma$ denotes the damping rate. In equation (9), $a^+, a$ are the creation/annihilation operators of a harmonic oscillator, defined through

$$a = \frac{1}{\sqrt{2}} \left( \sqrt{\frac{\hbar}{m\omega_c}} \hat{X} + i \frac{1}{\sqrt{\hbar m\omega_c}} \hat{P} \right). \tag{10}$$

Here, $\hat{X}$ and $\hat{P}$ are the usual position and momentum operators w.r.t. the harmonic oscillator minimum and $\omega_c$ its frequency. The quantum optical master equation (9) can be derived from a von Neumann equation for the full system and is valid only for weak couplings between the system and the ‘bath’ (which is the helium droplet here). Also, in the derivation one makes use of the Markov and rotating wave approximation. For a significant temperature, additional terms that describe thermal excitations from the environment have to be taken into account [65]. The damping constant $\gamma$ may in principle be derived from a microscopic description of the interaction between the system and the bath (Fermi’s golden rule). We do not specify this interaction, but use the damping rate $\gamma$ as a fit parameter to obtain agreement with experimental data. The master equation (9) induces the evolution of a pure initial state into a state mixture.

For the numerical propagation, we return from the density matrix description to a Schrödinger-type equation for the state vector. It is not possible to evolve a pure state into a mixed state with a deterministic Schrödinger equation. One therefore considers a stochastic differential equation for a state vector, quantum state diffusion (QSD) [66]. The density is recovered from the average over several realizations of state vectors. Given a master equation in the ‘Lindblad form’, as in our case, it is straightforward to state the corresponding QSD Ito stochastic Schrödinger equation for a state vector [66]:

$$\frac{d\psi(t)}{dt} = -\frac{i}{\hbar} H_\text{f} \psi \psi \psi dt + \frac{1}{2} \gamma (2\langle a^+ a - a^+ a - |\langle a|\rangle^2 \rangle \psi \psi \psi dt + \sqrt{\gamma}(a-\langle a\rangle)\psi \psi \psi d\xi(t). \tag{11}$$

The left-hand side means $|d\psi(t)| = |\psi(t + dt) - |\psi(t)\rangle$, i.e. the change of the state after a time increment $dt$. The second term induces transitions to lower-lying vibrational states. The third term is stochastic and contains complex normalized Ito increments $d\xi(t)$, which satisfy

$$d\xi^2 = (d\xi^*)^2 = 0,$$

$$d\xi \, d\xi^* = dt. \tag{12}$$

The increment of the density up to second order in $dt$ is given through $d\rho = |d\psi\rangle\langle\psi| + |\psi\rangle\langle d\psi| + |d\psi\rangle\langle d\psi|$. Since equation (11) is written in the Ito form, one can easily take the average with respect to (12) and prove the equivalence with the given master equation (9). Recovering the density $\rho = |\psi(t)\rangle\langle\psi(t)|$ from several realizations of $|\psi\rangle$ amounts to obtaining expectation values through $\langle A \rangle = \text{Tr}(A\rho) = \langle \psi | A | \psi \rangle$. In figure 5, we show the coordinate expectation value $\langle R \rangle$, obtained from a single realization of $|\psi\rangle$. The norm of the state in equation (11) is conserved, i.e. $d(\langle \psi | \psi \rangle) = 0$. However, due to the finite time step $\Delta t$, the norm can slightly fluctuate. Therefore, for the numerics, we impose norm preservation by renormalizing the state vector after every time step. After replacing the ladder operators in equation (11) through their definition in (10), the rhs is strictly separable into operators, which act in either momentum or coordinate space. Therefore, the split operator method [49] for the propagation of the WP can still be used, which is an advantage of this approach.

Helium-induced damping of vibrational WPs on a single electronic surface is described through equation (11), which is equivalent to the master equation (9) on average. In order
to obtain damping on several electronic surfaces, we propagate a full state vector $|\Psi(t)\rangle$ according to
\begin{equation}
|d\Psi(t)\rangle = -\frac{i}{\hbar}H|\Psi(t)\rangle dt + \sum_j \left[ D(\gamma_j) + \frac{i}{\hbar}\Delta_j \right] |\psi_j\rangle.
\end{equation}

The average is taken over several realizations of state vectors to recover the density via $\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$. Using a time step of $\Delta t = 1$ fs in the simulation, convergence is achieved after taking into account $N_r = 50$ realizations of state vectors. In equation (13), $D(\gamma_j)$ is the generalization of the rhs of equation (11) to obtain damping and accompanying fluctuations on an arbitrary surface,
\begin{equation}
D(\gamma_j) = \frac{1}{2} \gamma_j \left( 2\langle a_j^\dagger a_j - a_j^\dagger a_j - |\langle a_j\rangle|^2 \right) dt + \sqrt{\gamma_j} (a_j - \langle a_j\rangle) d\xi_j(t).
\end{equation}

In equation (14), all stochastic differential Wiener increments $d\xi_j$ are taken independently of each other. In the ladder operator of the surface $j$, one uses the position w.r.t. the respective harmonic oscillator minimum and its frequency. For most parts of the following, for simplicity, we set damping constants to be equal, $\gamma_j = \gamma$. However, we hasten to add that an interesting exception is provided in section 3.4. The agreement with experiment improves if one allows for undamped vibrational motion in the electronic ground state, $\gamma_0 = 0$. 

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The damping model provides an explanation for the signal decrease at $\lambda = 833$ nm (excitation scheme I). After several periods, vibrationally damped WPs on the $A$ surface no longer enter the initial FC region and therefore the ion yield decreases.

In figure 6, we depict the result of the damping model equation (13), using $\gamma_1 = 0.15$ ps$^{-1}$. Clearly visible is a shift of the central frequency $\omega_A \to \omega'_A > \omega_A$, since the WP relaxes to lower vibrational levels. A frequency shift is also observed experimentally [1]. In the full damping model, however, the signal decays to zero, since at this wavelength vibrational relaxation leads to a complete ‘closing’ of the initial FC window. This result is in contrast to the experimental observation, where a pronounced oscillation is also present at later delay times, see [1] and figure 2(b), and requires further studies below.

At $\lambda = 800$ nm (excitation scheme II), full damping leads to the result shown in figure 7(a). Through dissipation, the WP in the state $A^\dagger \Sigma_u^+ \equiv 1$ leaves the initial FC region. However, the decelerated WP approaches another FC window around the equilibrium distance, cf figure 5, after several circulations. The signal therefore shows a massive increase of the (shifted) frequency component $\omega'_A$.

For both excitation schemes, the inclusion of damping improves agreement with experiment for the first $\approx 10$ ps. However, at later times, there are still significant discrepancies. These can be removed by taking into account desorption of dimers off the droplet.

The clear visibility of both frequency components $\omega'_A$ and $\omega_X$ is again attributed to electronic decoherence: since the damping scheme is carried out (stochastically) independent of all involved electronic states, damping leads to electronic decoherence similar to the fluctuating shifts we assumed previously. The final signal is an incoherent mixture of electronic contributions, as previously considered through equation (6). However, a massive increase of the component $\omega'_A$ is not observed experimentally (compare figures 3(b) and 7(a)).

Desorption of the dimer off the droplet prevents full vibrational damping in the electronic ground or excited state. Indeed, as we will show, desorption implies the disappearance of the
Figure 7. Calculated spectra in the time–frequency domain at $\lambda = 800$ nm. (a) Full damping: the WP in the A state leaves the initial transition region; consequently, the component $\omega_A$ decreases. The fully damped WP, however, reaches a transition region at the equilibrium distance, such that $\omega_A$ returns. See also figure 5. (b) The state-dependent desorption model. (c) The state-dependent desorption model together with undamped motion in the ground state.

component $\omega_A$ and simultaneous ongoing presence of $\omega_X$. For excitation scheme I, desorption explains the observed signal oscillation at later delay times.

3.3. Desorption

The release of a dimer into the gas phase takes place at some random time $t'$. In our model, a state vector evolves according to equation (13) up to time $t'$. As the He influence vanishes at $t'$, shift/damping terms in equation (13) are set to zero. We have to consider the ion yield at delay time $\tau$, which is changed because of the disappearance of the He influence at time $t'$. If the desorption occurs before the decay of the probe pulse ($t' \lesssim \tau$) the resulting signal is denoted by $S(\tau, t')$. If the desorption occurs after decay of the probe pulse ($t' \gtrsim \tau$), the ion yield is unaffected by the desorption process. Anything that happens after the probe pulse will not be mapped to the ion yield. The resulting signal is denoted by $S(\tau, \tau)$.

Note that in an ensemble of attached dimers, the desorption time $t'$ will be distributed according to some probability distribution $P(t')$. We therefore have to calculate the pump–probe signal for various desorption times $t'$ and consider the averaged signal.

We first assume that the electronic state occupation is not relevant in the desorption process. A dimer therefore has a certain probability of staying on or leaving (still being in
the superposition) the droplet, but this probability is independent of the specific electronic occupation. We assume a constant probability
\begin{equation}
  p_{\text{off}}(t', t' + \Delta t') = \Delta t' R_D
\end{equation}
that the dimer leaves the droplet within a small time interval \((t', t' + \Delta t')\). Here, \(R_D\) marks the constant desorption rate. The probability of finding the dimer attached at arbitrary time \(t'\) is hence given by
\begin{equation}
  P_{\text{on}}(t') = e^{-t' R_D}.
\end{equation}

The signal contains weighted contributions and is obtained from
\begin{equation}
  \langle S(\tau) \rangle = R_D \int_0^\infty P_{\text{on}}(t') S(\tau, t') dt' \\
= P_{\text{on}}(\tau) S(\tau, \tau) + R_D \int_0^\tau P_{\text{on}}(t') S(\tau, t') dt'.
\end{equation}

In the second line, we have used that for \(t' \gtrsim \tau\) (desorption after decay of the probe pulse) the ion yield does not change. In this case, the dimer is fully damped until the probe pulse has passed.

In a previous study, we made use of the state-independent desorption scheme equation (17), see [2]. Although it is possible to find reasonable agreement with experimental findings, it is an oversimplification to not take into account the electronic state for desorption. It is likely that only electronically excited dimers leave the droplet. The electronic excitation implies a larger degree of distortion of the helium environment [44]. On the other hand, it is reasonable to assume that (slowly moving) ground-state systems stay attached. Therefore, we consider an alternative desorption scheme and only allow excited dimers to leave the droplet. Desorption is again described in terms of a constant in time desorption rate \(R_D\). The probability for the molecule to desorb, however, is now proportional to the excitation probability \(p_e = \sum_{i \neq 0} p_i\), such that equation (15) is replaced by
\begin{equation}
  p_{\text{off}}(t', t' + \Delta t') = p_e R_D \Delta t'.
\end{equation}

Note that in this scheme, the state after desorption does not contain any electronic ground-state component (see later). Those dimers that do not desorb evolve according to the dissipative dynamics equation (13). In order to compensate for apparent loss of ground-state dimers, we need a third possible channel: with probability \(p_g R_D \Delta t' = (1 - p_e) R_D \Delta t'\) the dimer remains on the droplet and is projected onto its electronic ground state. For the full averaged signal, we obtain
\begin{equation}
  \langle S_{SD}(\tau) \rangle = P_{\text{on}}(\tau) S(\tau, \tau) + p_e R_D \int_0^\tau P_{\text{on}}(t') S_e(\tau, t') dt' + p_g R_D \int_0^\tau P_{\text{on}}(t') S_g(\tau, t') dt'.
\end{equation}

\(S_e(\tau, t')\) is the signal obtained upon removal of the helium influence at time \(t' \lesssim \tau\) and subsequent projection on the excited superposition of electronic states. Likewise, \(S_g(\tau, t')\) is obtained upon projection on the ground state. Note that a renormalization of the full wave function \(|\Psi\rangle\) is required after projection, such that \(\sum p_i = 1\) is always valid.
In figure 6(b), we show the spectrogram for \( \langle S_{SD}(\tau) \rangle \) at \( \lambda = 833 \) nm (scheme I). We use a desorption rate \( R_D = 0.1 \) ps\(^{-1}\), while the damping/shift parameters are not changed (as before, \( \gamma = 0.15 \) ps\(^{-1}\) and \( \Delta_2 = -50 \) cm\(^{-1}\)). In the spectrogram, a (small) frequency shift is \( \omega_A \rightarrow \omega'_A \) is observable. The shift mainly due to contributions of vibrationally damped dimers by means of the first term in equation (19). We obtain a frequency shift \( \omega_A \rightarrow \omega'_A \) in the model, but the shift is more pronounced in the experiment [1]. The second term in equation (17) marks contributions from dimers which are damped up to time \( t' \lesssim \tau \), but are not damped afterwards, i.e. upon release from the droplet. Early desorbing dimers are not vibrationally relaxed and the WP in the \( A^1 \Sigma_u^+ \) state continues to reach the initial FC region. From this point of view, undamped dimers may well contribute to the ion yield. Indeed, contributions to the ion yield at later delay times \( t \gtrsim 20 \) ps are exclusively attributed to these undamped dimers. There, the oscillation frequency is near the initial gas-phase value \( \omega_A = \omega_{\tau,\tau+1} \). As a final note, we find that the observed frequency shift \( \omega_A \rightarrow \omega'_A \) becomes negligible if we do not include the electronic shift \( \Delta_2 \) in the model.

As the laser frequency is further increased, the vibrational energy of the WP in the \( A^1 \Sigma_u^+ \) state increases (scheme II). Due to the larger elongation and faster dynamics, one may think of larger damping of vibrational motion and/or faster desorption of dimers off the droplet. In figure 7(b), we show the spectrogram at \( \lambda = 800 \) nm, as obtained for \( \gamma_i = 0.15 \) ps\(^{-1}\) and \( R_D = 0.5 \) ps\(^{-1}\), i.e. we assume a faster desorption as before for scheme I. In fact, this value for the desorption rate means that dimers quickly leave the droplet after the pulse excitation. Until desorption, electronically excited dimers are fully damped. During that time, they approach an intermediate transition region with smaller overlap with higher electronic states, see figure 5(c). As a consequence, the component \( \omega_A \) fades away after several picoseconds. Also, vibrational WPs of desorbed dimers do not reach the FC window at the equilibrium distance, which is also marked in figure 5(c). Therefore, an increase of the component \( \omega_A \) is excluded, compare figures 7(a) and (b). To conclude, damping in connection with fast desorption of dimers explains the experimental result, see figure 3(b), where the component \( \omega_A \) is only visible in the beginning of the measurement and then disappears. Note that dimers which remain on the droplet in the ground state are fully damped. Therefore, the ground-state component \( \omega_X \) decreases in this model.

### 3.4. Undamped ground-state WPs

Agreement with experiment can be further improved if one allows for undamped motion of the vibrational WP in the ground state. This is of particular relevance for excitation scheme II, for which the result upon leaving the model parameters for damping, desorption and shift unchanged, but setting \( \gamma_0 = 0 \), is shown in figure 7(c). Frequency components at later delay times are exclusively attributed to the ground-state motion, i.e. the component \( \omega_X \) is clearly visible. Undamped vibrational WP motion has been discussed in terms of a critical Landau velocity \( v_{\text{crit}} \) in [2]. The existence of \( v_{\text{crit}} \) in the superfluid nanodroplet may allow for frictionless motion of slowly moving ground-state WPs. In figure 7(c), the ground-state motion is assumed frictionless; good agreement with the experimental result, see figure 3(b), is also obtained for nearly frictionless motion \( \gamma_0 \approx 0 \).

Note that for the observation of the ground-state WP, the electronic shift \( \Delta_2 \) is less important. It only leads to a slightly different ratio between the ground- and excited-state frequency components.
4. Conclusions

We consider vibrational WP dynamics of dimers attached to He nanodroplets. It is found that (calculated) gas-phase spectra and spectra from dimers attached to He droplets are markedly different. The interaction between droplets and dimers influences the vibrational dimer dynamics in three ways: shifts, damping and desorption. All three ingredients are taken into account in a phenomenological manner and each contributes to characteristic changes of the resulting spectra.

First, we study electronic decoherence, occurring for instance due to slightly fluctuating shifts of electronic surfaces. We find that, indeed, the resulting spectra do not show electronic interferences such that contributions from several electronic states, in particular the ground state, are clearly resolved. In this way, the modeled spectrum is already similar to the experimental finding.

However, pure electronic decoherence cannot explain a decreasing contribution to the signal from WPs in the first excited $A^1\Sigma^+_u$ state. Consequently, vibrational damping of WPs is taken into account, which improves agreement with experiment for short delay times. We find that damping is not present over the full observation timescale, probably due to desorption of dimers from the droplet. We use a desorption scheme, which takes into account the occupation of electronic levels. We find that the desorption rate depends on the mean vibrational energy of the WP. At $\lambda = 800$ nm, desorption is fast, taking place on average several picoseconds after excitation ($R_D = 0.5$ ps$^{-1}$).

Note that, in this study, all involved electronic states are spin singlet states. For the WP in these singlet states, we find a relaxation rate which is significantly higher than in previously considered spin triplet Rb$_2$ dimers attached to He droplets. The smaller rate in the latter may be ascribed to the orientation of the dialkali axis relative to the droplet surface. Recent calculations show that the axis of spin triplet dimers is oriented parallel to the droplet surface, while singlet states are assumed to be oriented perpendicularly [29, 67]. Upon the perpendicular orientation in our case, the dimer might interact with the droplet more efficiently, such that relaxation is faster.

Damping appears to be absent for (slowly moving) WPs in the electronic ground state. There, vibrational motion is found to be nearly frictionless. A potential energy surface for the dimer–droplet system, which is currently under way for Rb$_2$ [67], should give additional insight into dissipation rates of the WP.

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