

Coherent dynamics of small molecules in rare gas crystals

M. Gühr, AG Schwentner and Sfb 450
Institut für Experimentalphysik,
Freie Universität Berlin

The molecule Br_2 embedded in solid argon is investigated for the first time on the ultrashort domain via femtosecond pump-probe spectroscopy. Coherent intramolecular vibrational wave packet dynamics and coherent host dynamics are identified in the spectra. The electronic B state potential surface is constructed from the experimental periods using the RKR algorithm, and the energy relaxation is quantified over a large range in this state. During the first molecule-cage collision, up to 50 % vibrational energy loss of the wave packet is observed; however, the intramolecular coherence is preserved in the strong interaction. Furthermore, the coherence can even survive nonadiabatic electronic transitions, as is documented for the case of I_2 in solid Kr.

Interferences in vibrational wave packets of Br_2 molecules are controlled in the presence of a solid Ar environment that provides decoherence. A control scheme based on chirped pulses is worked out with help of a numerical wave packet propagation. By applying a negatively or positively chirped excitation pulse, one can set the clock backward or forward respectively in the wave packet propagation.

Based on this mechanism, we present a general scheme to record vibrational decoherence. Wave packets are spatially focused at T_{opt} by applying negatively chirped pulses. From the focusing contrast, we determine a vibrational dephasing time on the B state of $T_{\text{deph}}^{\text{vib}} = 3$ ps corresponding to about 11 vibrational periods, each of 280 fs. Positively chirped pulses advance the formation of fractional revival structures with respect to $T_{\text{deph}}^{\text{vib}}$. By exciting four vibrational levels with such a pulse in an experiment, we observe a 1/6 revival, indicating the vibrational coherence time $T_{\text{vib}}^4 \approx 1.2$ ps for exactly four levels. The required chirp prolongs the pulse duration by a factor of ten to $\Delta\tau = 300$ fs. Electronic dephasing $T_{\text{deph}}^{\text{el}}$ of the $\text{B} \leftarrow \text{X}$ transition restricts the revival control fidelity to parts of the pulse with $\Delta\tau < T_{\text{deph}}^{\text{el}}$, which allows for the determination of $T_{\text{deph}}^{\text{el}} > 300$ fs.

A long lasting coherent oscillation with a sharp frequency $f_{\text{P}} = 2$ THz is observed in $\text{Br}_2:\text{Ar}$ pump-probe spectra. It matches exactly the Zone Boundary Phonon (ZBP) frequency of the solid Ar host. Furthermore, a frequency component with $f_{\text{P}} = 1.5$ THz is observed in $\text{I}_2:\text{Kr}$ pump-probe spectra, matching the Kr crystal ZBP frequency. The value of f_{P} and its phase with respect to the pump pulse do not depend on the B or A state vibrational dynamics. The phonons originate from a Displacive Excitation of Coherent Phonons (DECP) initiated in the electronic $\text{B} \leftarrow \text{X}$ and $\text{A} \leftarrow \text{X}$ transitions. A model calculation shows that an expansion of the electronic density in going from the electronic ground state X to the B or A state kicks the Ar/Kr atoms in the Br_2/I_2 vicinity. Subsequently, a group of host atoms in the (100) plane is decoupled from the intramolecular dynamics. The ZBPs have a vanishing group velocity v_{g} , and therefore they stay in the vicinity of the chromophore, whereas phonons with longer wavelength propagate away from the molecule. The ZBP modulates the solvation energy of the terminal charge-transfer states used in the probe transition from the A and B state and thus the detection sensitivity of the intramolecular molecular wave packet.