Section 18.5:Effective two-electron systems of the form* Na_nF_{n-2}

Non-stoichiometric alkali halide molecules have provided versatile test cases for the assessing various methodologies for modeling pump-probe spectra. Units of higher complexity than the species Na_2F and Na_3F_2 discussed above have been investigated to explore the validity range of the semi-classical trajectory approach outlined in Sect. 18.4. In contrast to the effective single electron systems, the cluster Na_3F involves two active electrons, which poses a greater challenge to any attempt at representating of the relevant excited states and related potential energy gradients required for trajectory propagation *on the fly.* The task of simulating pump-probe signals for the experimentally studied Na_3F unit [42] has been confronted adopting two competing approximations [43]. More specifically, the trajectory based Liouville-von Neumann approach in conjunction with the impulsive approximation for the pump pulse has been compared with wave packet propagation on the relevant potential energy surfaces. The limitation of the latter technique consists in the high computational effort required to calculate these surfaces as well as the wave packet time evolution (see chapter 15). However, it may be possible to select a subset of nuclear coordinates representative of the problem at hand and thus to restrict its dimensionality, making the wave propagation procedure practicable. This has been demonstrated for Na_3F which adopts a C_{2v} ground state geometry as shown in Figure 18.15a. Lifted vertically into the third excited state, the cluster distorts into another C_{2v} structure, displayed in Figure 18.15(b). Three internal coordinates are required to describe the deformation that leads from the first to the second geometry, labeled ξ, η and R in Figure 18.15(c).

Applying time-dependent perturbation theory at first order, we obtain the excited state wave function in accordance with Eq. (18.23) as

$$\psi_1(R,\xi,\eta,t) = -\frac{i}{\hbar}\int_0^t dt' \exp(-\frac{i}{\hbar}\hat{H}_1(t-t'))[\mu_{01}\varepsilon_{pu}(t')]\exp(-\frac{i}{\hbar}\hat{H}_0 t') \\ \psi_0(R,\xi,\eta,t=0) \qquad (1)$$

Here $\hat{H}_i$, $i = 0, 1$, stands for the ground and third excited state Hamilton operator, respectively, where the adiabatic representation has been adopted. We define an envelope function $f(t)$ and make use of the rotating wave approximation, writing ε_{pu} as $\varepsilon_{pu}(t) = \frac{1}{2}\varepsilon^0_{pu}f(t)\exp(-i\omega_{pu}t)$. Assuming a vibrational energy E_0 as eigenvalue of $\hat{H}_0$ in the electronic ground state, an iteration scheme was applied to propagate the wave packet on the excited state surface. Explicitly:

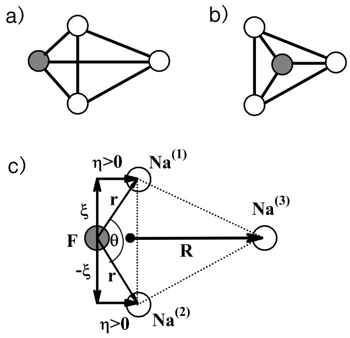

Figure 1: Figure 18.15 a,b,c: (a) The shape of the $\mathrm{Na_3F}$ cluster in its $1\ {}^1A_1$ electronic ground state and (b) in the third excited electronic state which has $1\ {}^1B_1$ symmetry. The wave packet propagation on the potential energy surface of the latter state is performed in a nuclear coordinate subspace given by the degrees of freedom ξ, η and R , as shown in (c). (Reprinted with permission from [44]. Copyright 2001 by the American Physical Society.)

$$\begin{aligned}\psi_1(R,\xi,\eta,t+\Delta t) = \exp(-\frac{i}{\hbar}\hat{H}_1\Delta t)\psi_1(R,\xi,\eta,t) - i(\frac{\Delta t}{2})\mu_{01}\varepsilon^0_{pu}f(t+\Delta t) \\ \times\exp[\frac{i}{\hbar}(E_0+\hbar\omega_{pu})(t+\Delta t)]\psi_0(R,\xi,\eta,t=0)\end{aligned} \tag{2}$$

The final state of the system, as generated by application of the probe pulse, consists of a Na_3F^+ ion and a free photoelectron. Assuming a complete and continuous set of basis functions $|E\rangle$, labeled according to the energy of the electron, we may expand the final wave function $|\Psi_{ion}\rangle$ according to

$$|\Psi_{ion}\rangle = \int dE\ \psi^{ion}_E|E\rangle \tag{3}$$

In analogy to Eq.(1), we describe the wave function of the ionic system by the expression

$$\begin{aligned}\psi^{ion}_E(R,\xi,\eta,t;t_d) = -\frac{i}{\hbar}\int_{-\infty}^{t} dt'\exp(-\frac{i}{\hbar}(\hat{H}_2+E)(t-t'))[\mu_{21}\varepsilon_{pr}(t'-t_d)] \\ \times\exp(-\frac{i}{\hbar}\hat{H}_1(t'-t_d))\psi_1(R,\xi,\eta,t_d),\end{aligned} \tag{4}$$

where the delay time t_d between the pump and the probe pulse has been introduced, and the index 2 refers to the cationic level. The interaction between the cation and the free electron is not taken into account by this formula. For the probe pulse, a central frequency ω_{pr} is adopted, and thus $\varepsilon_{pr}(t) = \frac{1}{2}\varepsilon^0_{pr}F(t)\exp(-i\omega_{pu}t)$, with $F(t)$ as the appropriate envelope function. As in the case of the pump pulse $\varepsilon_{pu}(t)$, this function may conveniently be chosen as a Gaussian, however, it is worth mentioning that the perturbative scheme portrayed here makes admission for general pulse shapes. Summarizing Eqns.(1), (3), and (4), we arrive at a total ion signal given by

$$S(t_d) \sim \lim_{t\to+\infty}\int_0^\infty dE\int dRd\xi d\eta\ |\psi^{ion}_E(R,\xi,\eta,t;t_d|^2 \tag{5}$$

It is instructive to compare the results yielded by the semiclassical method based on Eq.(105) and the dimensionally reduced wave packet propagation treatment for $NeExPo$ spectroscopy applied to an initially thermal Na$_3$F ensemble. Figure 18.16a-c shows the experimental findings at a probe pulse energy of $E_{pr} = 2.04 - 2.08$ eV [42]. These data are to be compared with the semiclassical simulation in Figure 17.16a and the quantum wave packet computation in Figure 17.16b. For the latter, the configuration interaction (CI) formalism has been used to calculate the relevant potential energy surfaces.

The oscillations recorded by pump=probe spectroscopy are associated with a near-periodic alternation between the two C_{2v} shapes displayed in Figure

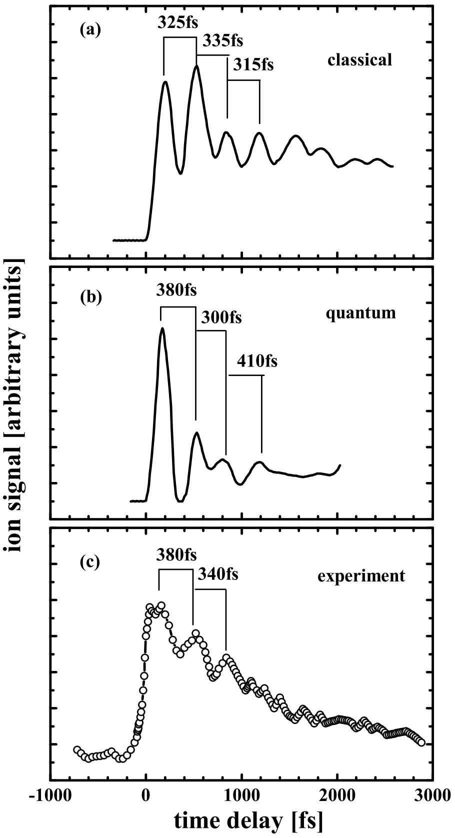

Figure 2: NeExPo signals obtained for Na_3F at a probe laser energy E_{pr}= 2.05 eV [44]. Panel (c) shows the experimental finding [42]. This is compared with the result of a trajectory based simulation in (a) and wave packet propagation in (b).(Reprinted with permission from [44]. Copyright 2004 by the American Institute of Physics.)

18.16 (a) and (b). Both computational procedures capture the essential features recorded in experiment. The deviations from the measured results, however, reveal the characteristic shortcomings of the two approaches, and these naturally reflect the assumptions on which the models are based. Thus, the trajectory method relies on the impulsive approximation, resulting in a trajectory ensemble on the excited state whose energy spread overestimates the respective experimental energy dispersion. The energy filtering property of a laser pulse with finite duration leads to an excited state energy distribution whose width scales with the inverse of the pulse duration, its maximum being located at the central laser frequency. The semi-classical scheme neglects this mechanism, and the background of the ion signal seen in Figure 18.16(a) emerges as a consequence of this simplification. Due to the unrealistically enhanced range of energies present in the ensemble, a considerable fraction of trajectories matches the condition for transition from the third excited to the ionized level of Na_3F at any time during the evolution of the system.

While the wave packet propagation method is free of the deficiency that plagues the phase space model, i.e. a lack of energy selectivity affecting the accuracy of the excited state dynamics, its inherent dimensional restriction obviously narrows its scope of validity. For the case considered here, i.e. the motion of $\mathrm{Na_3F}$ on the third excited state surface, comparison with the full-dimensional semiclassical treatment confirms that deviations of the system from C_{2v} symmetry are extremely slight during the first picosecond of propagation [44], justifying for this initial period the adequacy of the geometric constraints shown in Figure 18.15c. For longer times, however, the remaining vibrational modes of the cluster become more prominent, and the reduced dimensionality may act as a severe methodological limitation.

As is plausible from the foregoing discussion, the two procedures used to compute the $Na_3FNeExPo$ signal are, to a large extent, complementary. The phase space propagation method encompasses the full dimensionality of the problem, but suffers from an overestimation of the trajectory energy spread, giving rise to an artificial background that deteriorates the simulation quality. Dimensionally reduced wave packet propagation, on the other hand, combines good energy selectivity with a potentially unrealistic restriction imposed on the number of active degrees of freedom.

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