TIME DOMAIN NONADIABATIC DYNAMICS OF NO_2

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This work deals with the time domain nonadiabatic dynamics of NO_2 on the first two electronics states, X^2A_1 and A^2B_2.
We first present the evolution at short times (below 200 fs), obtained by launching quantum wave packets on both electronic surfaces, and show that electronic populations evolve through a series of plateaux that can easily be interpreted and reproduced using quasi-classical techniques. Moreover, we propose a simple diabatic surface hopping model which enables a good estimation of complex quantities, such as the projection of the instantaneous probability density on each diabatic electronic surface.
We then point out that this quasi-classical regime is followed at longer times by a purely quantum mechanical regime of slow periodic oscillations, which are clearly observed in the evolution of electronic populations and of the squared modulus of the autocorrelation function $|A(t)|^2$. We show that the oscillations in electronic populations are due to the intramolecular vibronic energy transfer caused by the electronic coupling. This is also the case for the oscillations of $|A(t)|^2$ when the wave packet is launched with an energy not too high compared to that of the bottom of the conical intersection, but this is no longer true at much higher energies. In particular, we show that for a wave packet prepared by an almost vertical excitation of the vibrational ground state of the X^2A_1 electronic state, oscillations of $|A(t)|^2$ essentially reflect the detuning from $1:2$ resonance between the frequency of the bend and that of the symmetric stretch in the excited electronic state. These results are used to discuss the possible origin of low frequency oscillations recently observed in pump-probe experiments on NO_2.

[1] M. Sanrey and M. Joyeux, J. Chem. Phys. 125, 014304 (2006)
[2] M. Sanrey and M. Joyeux, J. Chem. Phys. 126, 074301 (2007)