

# Simulation of the photodissociation of vibrationally pre-excited pyrrole and deuterated pyrrole molecules with *ab initio* multiple cloning approach

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We present the simulations of the photo-dissociation dynamics for vibrationally pre-excited pyrrole [1] and deuterated pyrrole [2] molecules using the *ab initio* multiple cloning (AIMC) computational approach [3] that has proven its efficiency in our previous simulations for pyrrole [4] and other heterocyclic molecules [5,6]. The AIMC makes use of the basis of Gaussian coherent states moving along a set of branching Ehrenfest trajectories. The initial positions and momenta are taken random with the probability distribution adjusted to consider the initial pre-excitation of particular vibrational modes.

Calculations show that pre-excitation of N–H bond vibrations in pyrrole molecule facilitates the process of fast direct dissociation, which results in a significant increase in the high-energy wing of total kinetic energy release (TKER) spectrum. These results are in good qualitative agreement with the recent vibrationally mediated photodissociation experiment [7], where the TKER spectrum was measured for pyrrole molecules excited by a combination of IR and UV laser pulses. We demonstrate that this effect is specific for N–H bond vibrations: pre-excitation of other vibrational modes does not result in any significant changes in TKER spectra.

Our calculations of photo-dissociation kinetics predict that pre-excitation of N–H bond vibrations should result in a lower dissociation time due to a significant increase in the dissociation rate in the first moments after electronic excitation, while the rate at later times remains practically unchanged.

In order to study the isotopic effect, we also run photodissociation dynamics simulations for deuterated pyrrole molecules. Similar to the case of pyrrole, the pre-excitation of N–D bond vibrations in deuterated pyrrole significantly facilitates the process of fast direct

photodissociation, while the pre-excitation of other vibrational modes has practically no effect on the photodissociation dynamics. The kinetic energy of additional dissociation fragments is lower for deuterated pyrrole and mostly located in the upper-middle part of the TKER spectrum, which can be explained by lower energy of dissociative bond vibrations. Nevertheless, the integral increase of the dissociation yield is much higher for deuterated pyrrole. Also, kinetics simulations show that pre-excitation of N–D bond vibrations reduces more than by half the dissociation time of deuterated pyrrole, significantly more than for pyrrole. These computational predictions are waiting for an experimental confirmation, and we hope that our numerical results may encourage future VMP experimental studies for pyrrole and other similar molecules.

**Index Terms:** photodissociation, pyrrole, non-adiabatic dynamics, simulation.

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