

Are artificial neural networks useful to describe the non-adiabatic dynamics of the nitrate radical ?

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The nuclear dynamics and spectroscopy of the NO₃ radical is still not fully understood despite multiple theoretical and experimental investigations over the last decades. Experimentally, the Neumark group made two breakthroughs by recording in 1991 [1] the first photodetachment spectra of the nitrate anion (NO₃⁻) and in 2020 by providing a cryogenic cooling version of these spectra [2]. Their interpretation requires a detailed and complete modelling of the five lowest potential energy surfaces of the radical.

We propose a scheme to simulate the photodetachment spectrum of the nitrate anion from first principles. It relies on the determination of accurate full-dimensional coupled diabatic potential energy surfaces adjusted to high quality ab initio energies via an artificial neural network based scheme [3]. The Multi-Configurational Time Dependent Hartree approach is used to propagate full dimensional wave-packets designed such that temperature effects and the impact of near threshold detachment are taken into account [4].

The two available experiments at high temperature and at cryogenic temperature can be reproduced in very good agreement. These results clearly show the relevance of hot bands as well as vibronic coupling between the ground state and the second excited state of the neutral radical. This together with the recent experiment at low temperature gives further support for the assignment of the ν_3 fundamental of neutral NO₃. A not yet discussed hot band line is also assigned. A study at higher the energy range is also proposed [5].

[1] A. Weaver, et al.; *J.Chem.Phys.* **94** 1740 (1991)

[2] M.C. Babin, et al.; *J.Phys.Chem.Lett.* **11** 395 (2020)

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[4] A. Viel, D.M.G. Williams, W. Eisfeld; *J.Chem.Phys.* **154** 084302 (2021)

[5] D.M.G. Williams, W. Eisfeld, A. Viel; *Phys.Chem.Chem.Phys.* **24** 24706 (2022)