Photodetachment spectrum of NO_3^-: Jahn-Teller effect and artificial neural network

Alexandra Viel,[1] **David M. G. Williams**,[2] **and Wolfgang Eisfeld**[2]

[1]*Institute of Physics of Rennes, UMR 6251 CNRS & Université Rennes 1, Rennes, France*
[2]*Theoretische Chemie, Universität Bielefeld, Bielefeld, Germany*

Detailed and fundamental understanding of the nuclear dynamics of the NO_3 radical stays enigmatic despite multiple theoretical and experimental investigations over the last years. Experimentally, the Neumark group made two breakthroughs by recording in 1991 [1] the first photodetachment spectra of the nitrate anion (NO_3^-) and in 2020 by providing a cryogenic cooling version of these spectra [2]. The interpretation of the spectra requires a detailed and complete modeling of the five lowest potential energy surfaces of the NO_3 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 quantum dynamics simulations based on full dimensional wave-packet propagations are 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 using the slow electron velocity-map imaging technique (cryo-SEVI) can be reproduced in very good agreement. These results clearly show the relevance of hot bands as well as vibronic coupling between the $\tilde{X}\ ^2\mathrm{A}_2'$ ground state and the $\tilde{B}\ ^2\mathrm{E}'$ excited state of the neutral radical. This together with the recent experiment at low temperature gives further support for the proper assignment of the ν_3 fundamental, which has been debated for many years. An assignment of a not yet discussed hot band line is also proposed.

[1] A. Weaver, D.W. Arnold, S E. Bradforth, and D.M. Neumark *J. Chem. Phys.* **94**, 1740 (1991)

[2] M.C. Babin, J.A. DeVine, M. De Witt, J.F. Stanton and D.M. Neumark *J. Phys. Chem. Lett.* **11**, 395 (2020)

[3] D.M.G. Williams and W. Eisfeld *J. Chem. Phys.* **149**, 204106 (2018)

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