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Editor
The Journal of Chemical Physics

Dear Editor,

The following manuscript is for your consideration for publication in The Journal of Chemical Physics:

Title:	*Velocity Map Imaging Spectroscopy of C_2H^- and C_2D^-: a benchmark study of vibronic coupling interactions*		
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Conflict of Interest	The authors declare no competing financial interest.		

Significance

This research uses High Resolution Photoelectron Imaging (HR-PEI) to examine complex vibronic coupling effects in the ethynyl radical C_2H. Monohydride carbon chains play an important role in combustion and interstellar chemistry, with C_2H reported to be one of the most abundant molecules in the universe. However, these radicals are exceedingly difficult to model, due to the introduction of vibronic coupling interactions between the close lying $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ electronic

states. As our knowledge of interstellar chemistry relies critically on theory, a new approach is required that can both accurately model the complexity of the coupled spectra, and be efficiently extended to larger $C_{2n}H$ radicals.

In this paper we apply a quasidiabtaic approach to construct a QVC (quadratic vibronic coupling) model Hamiltonian to account for the Renner-Teller and pseudo Jahn-Teller coupling in C_2H. We show how the Hamiltonian can be parameterised using the outputs of standard quantum chemical *ab-initio* calculations, to simulate the vibronic coupling effects in the photoelectron spectrum of C_2H and C_2D. Comparisons to the HR-PEI experimental spectra confirm that the QVC model accurately reproduces the coupling effects observed near the $\tilde{A}^2\Pi$ state origin. Anion HR-PEI spectroscopy maps both of the $\tilde{X}^2\Sigma^+$ and $\tilde{A}^2\Pi$ surfaces on an equal footing from the anion $\tilde{X}^1\Sigma^+$ state, allowing for a direct comparison with the *ab-initio* modelling. We also show that detailed analysis of the experimental electron anisotropy allows for transitions with σ and π vibronic symmetry to be distinguished, providing definitive assignments of the calculated transitions.

As the QVC quasidiabatic model can be readily extended to larger systems, this work provides a roadmap for future studies to follow, which will help to determine the role of $C_{2n}H$ and $C_{2n}H^-$ in interstellar chemistry.

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Statement

This manuscript is not being considered by any other journal.

Regards,
Dr Benjamin A. Laws.