

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Paul Burrow Publications

Research Papers in Physics and Astronomy

2014

Comment on 'Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres'

Paul Burrow

Gordon A. Gallup

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsburrow>



Part of the [Atomic, Molecular and Optical Physics Commons](#)

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Paul Burrow Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

COMMENT • OPEN ACCESS

Comment on 'Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres'

To cite this article: P D Burrow and G A Gallup 2014 *New J. Phys.* **16** 028001

View the [article online](#) for updates and enhancements.

Related content

- [Reply to Comment on 'Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres'](#)
F Carelli, M Satta, F Sebastianelli et al.
- [An investigation of electron helicity density in bromocamphor and dibromocamphor as a source of electron circular dichroism](#)
A M Scheer, G A Gallup and T J Gay
- [Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres](#)
A Garcia-Sanz, F Carelli, F Sebastianelli et al.

Recent citations

- [Low energy electron impact resonances of anthracene probed by 2D photoelectron imaging of its radical anion](#)
Golda Mensa-Bonsu *et al*
- [Reply to Comment on 'Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres'](#)
F Carelli *et al*

Comment on ‘Dynamics of formation of anthracene anions in molecular clouds and protoplanetary atmospheres’

P D Burrow¹ and G A Gallup

Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, NE
68588-0299, USA
E-mail: pburrow@unl.edu

Received 21 May 2013, revised 24 May 2013
Accepted for publication 26 November 2013
Published 7 February 2014

New Journal of Physics **16** (2014) 028001

[doi:10.1088/1367-2630/16/2/028001](https://doi.org/10.1088/1367-2630/16/2/028001)

Abstract

The shape resonances computed in the title paper are shown to be approximately 1.8 eV too high.

Garcia-Sanz *et al* [1] describe electron scattering calculations on anthracene in the gas phase and report the energies of seven temporary negative ion states, i.e. shape resonances, associated with electron attachment into the normally unoccupied π^* molecular orbitals. The calculations were carried out at the ground state geometry of the neutral molecule, and thus the resonance energies represent the vertical attachment energies (VAEs) of the neutral. The purpose of this comment is to point out that their energies do not agree well with experiment [2] or with energies obtained from semi-empirical scalings of computed virtual orbital energies (VOEs), an approach that has been extensively and successfully used to identify resonances and their symmetries for a number of years. The energies of [1] lie too high by approximately 1.8 eV.

Table 1 summarizes the relevant information. It suffices to consider only the lowest three π^* anion states of anthracene. The orbital symmetries of these are indicated, along with VOEs computed using the Hartree–Fock approach with a 6-31G(d) basis and geometry optimization at the same level. Comparisons of calculated π^* VOEs with VAEs measured by electron transmission spectroscopy (ETS) [3] by several groups have shown that excellent correlations between these energies exist. By shifting and scaling VOEs to match VAEs over a given

¹ Author to whom any correspondence should be addressed.



Table 1. The VAEs of anthracene. All values in eV.

Orbital	VOE (HF)	Scaling A	Scaling B	PPP	Exp. (ETS)	Garcia-Sanz <i>et al</i> [1]
$\pi_1^*(b_{3u})$	1.9238	-0.52	-0.18	-0.49	<0	1.16
$\pi_2^*(a_u)$	3.3171	0.53	0.65	0.65	0.60	2.46
$\pi_3^*(b_{1g})$	4.3892	1.34	1.28	0.92	1.13	2.91

‘training set’ of molecules, one can predict the VAEs and symmetries of other members of these families with good accuracy from their calculated VOEs. It is important to realize that this semi-empirical correction accounts *in an average sense* for precisely those properties that are the most difficult to calculate from first principles, namely, the additional correlation introduced by the presence of the added electron and for the coupling to the continuum, neither of which is included in the Koopmans’ VOE. For the present purpose, we show the results of scaling the VOEs of anthracene using two different molecular training sets, labeled scalings A [4] and B [5], determined by the Nebraska group. Scaling A, $VAE = (VOE - 2.61)/1.33$, is based on the lowest empty orbitals of benzene, pyridine, pyrimidine and naphthalene. The equation differs slightly from that in the reference owing to the use of the 6-31G(d) basis set for geometry optimization in the present work. Scaling B, $VAE = (VOE - 2.22)/1.69$, was obtained from a series of molecules with alternating phenyl and acetylenic groups. We include as well in table 1 the earlier PPP [6] predictions used to interpret the ETS results [2]. All energies are expressed in eV.

All the semi-empirical methods agree that the anion associated with the lowest empty orbital, b_{3u} , has negative energy, that is, it corresponds to a *vertically bound* anion state, consistent with the measured adiabatic electron affinity of 0.53 eV [7]. In contrast, the calculations of Garcia-Sanz *et al* [1] find it as a b_{3u} resonance at 1.16 eV which they associate with the lowest observed resonance at 0.60 eV, in spite of the energy discrepancy and the identification of this feature as an a_u resonance by Burrow *et al* [2] based on the PPP calculations. In fact, both scaled values and that from PPP corresponding to the a_u symmetry agree well with the experimental determination of the energy of the lowest resonance.

If we assume that the adiabatic and vertical electron affinities of anthracene do not differ substantially, then the *spacings* between the anion states of [1] are in rough agreement with those found experimentally. Thus it appears that the calculated anion states of [1] all lie approximately 1.8 eV too high. Such discrepancies have occurred in other studies by Gianturco and co-workers. For example, and choosing from more recent work, Goumans *et al* [8] locate the π^* resonance in formamide at 3.77 eV, whereas the ETS value [9] is 2.05 eV, a difference of 1.72 eV. Scaled VOEs of *o*-benzynes and coronene indicate that the calculated anion states of Carelli *et al* [10, 11] are too high by approximately 1.5 eV. While we can appreciate the difficulties in carrying out *ab initio* calculations of scattering cross sections in complex molecules, it is risky to assume at this time that the computed resonance energies will be as reliable as those given for the π^* anion states by the semi-empirical approach. Furthermore, drawing conclusions about mechanisms in which the putative b_{3u} resonance ‘evolves’ into a stable anion state of the same symmetry [1, 10] seems premature. Since submission of this comment, Gallup [12] has calculated the low-lying shape resonance energies of anthracene and six other planar compounds using the *ab initio* finite element discrete model. He found good agreement with the experimental energies and the scaled virtual orbital values discussed here.

Finally, returning to [1], Garcia-Sanz *et al* have misquoted the anthracene ETS energies given in [2] as well as the journal in which they were presented. The correct reference is given here.

References

- [1] Garcia-Sanz A, Carelli F, Sebastianelli F, Gianturco F A and Garcia G 2013 *New J. Phys.* **15** 013018
- [2] Burrow P D, Michejda J A and Jordan K D 1987 *J. Chem. Phys.* **86** 9
- [3] Sanche L and Schulz G J 1972 *Phys. Rev. A* **5** 1672
- [4] Aflatooni K, Gallup G A and Burrow P D 1998 *J. Phys. Chem. A* **102** 6205
- [5] Scheer A M and Burrow P D 2006 *J. Phys. Chem. B* **110** 17751
- [6] Younkin J M, Smith L J and Compton R N 1976 *Theor. Chim. Acta (Berl.)* **41** 157
Compton R N, Yoshioka Y and Jordan K D 1980 *Theor. Chim. Acta (Berl.)* **54** 529
- [7] Scheidt J and Weinkauff R 1997 *Chem. Phys. Lett.* **266** 201
- [8] Goumans T P M, Gianturco F A, Sebastianelli F, Baccarelli I and Rivail J L 2009 *J. Chem. Theory Comput.* **5** 217
- [9] Seydou M, Modelli A, Lucas B, Desfrancois C and Schermann J P 2005 *Eur. Phys. J. D* **35** 199
- [10] Carelli F, Sebastianelli F, Baccarelli I and Gianturco F A 2010 *Astrophys. J.* **712** 445
- [11] Carelli F and Gianturco F A 2011 *Astrophys. J.* **743** 151
- [12] Gallup G A 2013 *J. Chem. Phys.* **139** 104308