

BRIEF REPORT | OCTOBER 10 2023

Note: Photoelectron imaging of MnO_3^- to probe its nuclear and electronic structure

Jemma A. Gibbard ; Jonathan Reppel ; Jan R. R. Verlet 



J. Chem. Phys. 159, 146101 (2023)

<https://doi.org/10.1063/5.0171346>



Export
Citation

CrossMark

The Journal of Chemical Physics

Special Topic: Algorithms and Software for Open Quantum System Dynamics

Submit Today

Note: Photoelectron imaging of MnO_3^- to probe its nuclear and electronic structure

Cite as: J. Chem. Phys. 159, 146101 (2023); doi: 10.1063/5.0171346

Submitted: 8 August 2023 • Accepted: 18 September 2023 •

Published Online: 10 October 2023



Jemma A. Gibbard,^{a)} Jonathan Reppel, and Jan R. R. Verlet

AFFILIATIONS

Department of Chemistry, Durham University, Durham DH1 3LE, United Kingdom

^{a)} Author to whom correspondence should be addressed: jemma.gibbard@durham.ac.uk

© 2023 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/5.0171346>

Using anion photoelectron spectroscopy, a previous study by Gutsev *et al.*¹ found the ground state of MnO_3 to have a trigonal pyramidal structure. In this note, we revisit the MnO_3^- photoelectron spectrum using photoelectron imaging and reassess the assignment, showing that in fact, MnO_3 is planar in its ground electronic state. Furthermore, the photoelectron angular distributions (PADs) associated with electron emission to the neutral ground state provide insight into the highest occupied molecular orbital (HOMO) of the anion, showing that it is of predominantly Mn d_{z^2} character. All these results agree with a simple d-block model and are further supported by electronic structure calculations.

The geometric and electronic structure of transition metal complexes are often complicated by a high density of states, electronic state degeneracy, and the potential for isomers of similar energy, with additional factors such as relativistic effects and spin-orbit coupling also contributing complexity, particularly for the second and third row transition metals.^{2,3} As a result, geometry optimisation and electronic structure calculations can be challenging and can lead to unreliable results. Therefore, it is appealing to use simple models, such as the d-block model, which considers the relative ordering of the anti- and non-bonding d-orbitals on the transition metal centre within a ligand field, to propose likely structures.^{4,5} In an earlier study on a series of manganese oxides by Gutsev *et al.*, MnO_3 was determined to have a trigonal pyramidal (C_{3v}) structure through the use of anion photoelectron spectroscopy and electronic structure calculations, although no Franck-Condon simulations were presented.¹ This result is unusual as transition metal complexes with three ligands are normally trigonal planar (D_{3h}), as is the case for its anion MnO_3^- .⁴ Here, we have repeated these experiments using anion photoelectron imaging and electronic structure calculations on MnO_3^- and MnO_3 .

Anion photoelectron spectroscopy is a powerful tool for determining structural information about anions and their neutral counterparts, and has been applied to many transition metal complexes.^{1,5-12} Determination of nuclear geometries is enabled through agreement of the experimental photoelectron spectra and simulated Franck-Condon spectra based on electronic structure calculations. As a representative example, structural isomers of Ti_2O_4 and Zr_2O could be determined by high-resolution, cryogenic slow electron velocity map-imaging.⁹ Furthermore, the PAD, often quantified by the anisotropy parameter β_2 that runs from -1 to $+2$, can give electronic structure information of the anion.¹³⁻¹⁵ This approach has been used across a broad range of anions, including organic and inorganic species.¹⁶⁻¹⁸ In contrast, photoelectron imaging studies of transition metal anions have been relatively scarce,^{5,8,10,19-21} despite their aid in assigning electronic configurations.

The experimental apparatus has been described in detail elsewhere and will only be summarised here.^{22,23} MnO_3^- was produced via electrospray ionization of a 5 mM solution of KMnO_4 in acetonitrile. Anions entered the apparatus via a capillary, before being guided and trapped using a series of RF guides and subsequently accelerated to 2.2 kV using a Wiley McLaren time of flight spectrometer.²⁴ Mass selected anions were intersected with the variable wavelength output of a nanosecond optical parametric oscillator pumped via the third harmonic of a Nd:YAG. Ejected photoelectrons were focused onto the position sensitive microchannel plate and phosphor screen detector using a velocity map imaging setup. From the resulting images, the electron kinetic energy (eKE) and PADs were extracted following processing via the polar onion peeling algorithm.²⁵ Photoelectron imaging was performed at $h\nu = 3.76$ and 3.94 eV ($\lambda = 330$ and 315 nm), to determine how the spectral features shift with wavelength.

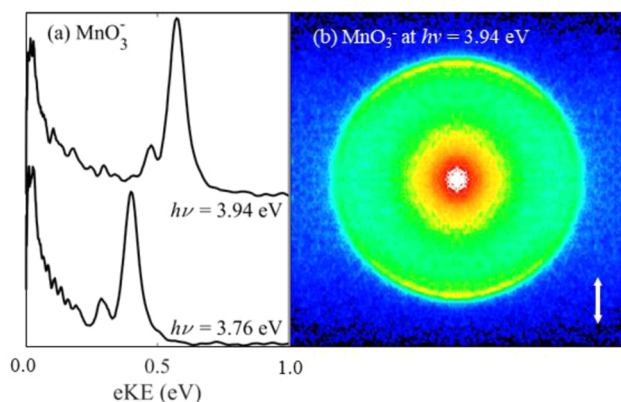


FIG. 1. (a) Photoelectron spectrum of MnO_3^- recorded at $h\nu = 3.76$ and 3.94 eV ($\lambda = 330$ and 315 nm) and (b) the photoelectron image MnO_3^- at $h\nu = 3.94$ eV ($\lambda = 315$ nm), with the polarisation vector of the light indicated by the double arrow.

Electronic structure calculations were also performed using density functional theory (DFT) at the B3LYP, TPSSh and PBE0 level of theory with the aug-cc-pVTZ basis set.^{26–29} Previously reported electronic structure calculations¹ used the BPW91 level of theory and the 6-311+G(d) basis set.^{30–33} These calculations were repeated and expanded upon here. Geometry optimisations were performed, molecular orbitals visualised, and Franck–Condon factor simulations undertaken. All calculations were performed using Gaussian 16.³⁴

Figure 1 shows the photoelectron spectrum of MnO_3^- recorded at $h\nu = 3.76$ and 3.94 eV, as well as the raw symmetrised photoelectron image of MnO_3^- at the higher photon energy. Two distinctive features are seen in the photoelectron spectra: a feature peaking near $\text{eKE} = 0$ eV with an exponentially decaying distribution; and a series of narrow peaks that shift with photon energy, the most intense peak of which is centred at a fixed, $\text{eBE} = h\nu - \text{eKE} = 3.37 \pm 0.05$ eV. From the photoelectron image in Fig. 1(b), the feature peaking at $\text{eKE} = 0$ eV is isotropic, whereas the higher energy features have an anisotropic PAD characterised by $\beta_2 = 1.5 \pm 0.25$.

The feature peaking at $\text{eKE} = 0$ eV has all the characteristics of thermionic emission, corresponding to electron loss from internally hot anions in their electronic ground state. The presence of thermionic emission indicates that there is rapid internal conversion back to the ground state following absorption of a photon to an excited state, with electrons then “boiling” off from the hot anions that have returned to the ground state. Such features have been seen in many other molecular anions,^{35,36} but it was not clearly observed by Gutsev *et al.*, although a gradual increase in signal near $\text{eKE} \sim 0$ eV was seen.¹ This difference is likely due to the fact that the previous photoelectron spectrum was acquired at $h\nu = 4.66$ eV ($\lambda = 266$ nm) and utilised a magnetic bottle spectrometer, which does not efficiently detect low eKE electrons. We note that our peaks are broader than those from Gutsev *et al.* (red, Fig. 2), which is likely as a result of the lower energy resolution of our photoelectron spectrometer (5% vs 3%).¹ Additionally, we do not observe the hot band presumably because of the methodology used to produce the anions (pulsed laser vaporization in a molecular beam, which

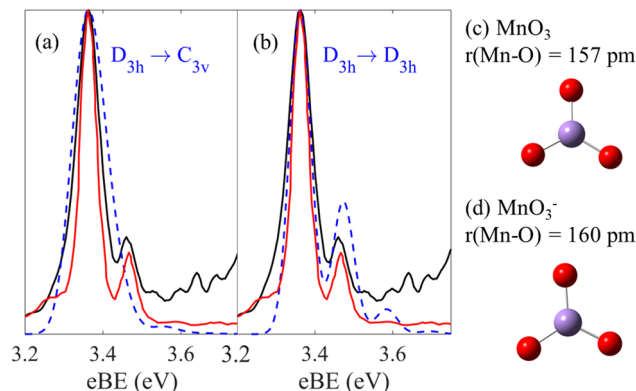


FIG. 2. The simulation of the Franck–Condon envelopes (blue) for (a) planar to pyramidal [BPW91/6-311+G(d)] and (b) planar to planar (B3LYP/aug-cc-p-VTZ), compared to the spectrum recorded at $h\nu = 3.94$ eV ($\lambda = 315$ nm) (black, also shown in Fig. 1) and the previously reported $h\nu = 4.66$ eV ($\lambda = 266$ nm) spectrum reported by Gutsev *et al.* (red, reprinted with permission from Gutsev *et al.* J. Chem. Phys. **113**, 1473 (2000). Copyright 2000 AIP Publishing LLC. The optimised structure of the planar (c) MnO_3 and (d) MnO_3^- used in the Franck–Condon simulations.

often leaves vibrational excitation, vs electrospray ionisation, which produces room temperature ions).

The feature with the dominant peak at $\text{eBE} = 3.37$ eV is attributable to direct detachment resulting in different vibrational energy levels of MnO_3 , with a second peak in the vibrational progression observed 0.1 eV lower in eKE . Gutsev *et al.* assigned the vibrational structure to the symmetric Mn–O stretch in MnO_3 , which they predicted to have a pyramidal (C_{3v}) geometry with a 117° bond angle, at the BPW91/6-311+G(d) level of theory,¹ while MnO_3^- was found to be planar (D_{3h}). All our calculations confirm that the anion is trigonal planar, however our geometry optimisations for MnO_3 result in both pyramidal and trigonal planar structures depending on the functional used. PBE0 predicts a pyramidal (C_{2v}) structure with a 118° bond angle, TPSSh predicts an effectively planar geometry ($>119.5^\circ$ bond angle) and B3LYP predicts a trigonal planar (D_{3h}) structure. The relatively narrow spectral peaks, and small amount of vibrational excitation left in the neutral, would appear to be inconsistent with a geometry change upon photodetachment from D_{3h} to C_{3v} , where one might anticipate significant Franck–Condon activity in the umbrella mode of MnO_3 that would broaden the observed photoelectron peaks.

To enable direct comparison with experiment, Franck–Condon simulations were performed based on the optimised geometries calculated using different functionals. The results using BPW91/6-311+G(d) and B3LYP/aug-cc-p-VTZ are shown in Figs. 2(a) and 2(b), respectively, where we have included a Gaussian convolution to account for the spectral resolution of our experiment (full-width-at-half-maximum is 25 meV). The $D_{3h} \rightarrow D_{3h}$ photodetachment [Fig. 2(b)] shows a vibrational progression, associated with the symmetric Mn–O stretch, with a spacing of 927 cm^{-1} (0.11 eV). In contrast, the spectrum calculated for a geometry change from $D_{3h} \rightarrow C_{3v}$ photodetachment has a series of low frequency modes [spacing of 160 cm^{-1} (0.02 eV)], associated with the out-of-plane umbrella motion of MnO_3 , resulting in a broadened spectrum as

shown in Fig. 2(a). The geometry of MnO_3 was crucial in determining the simulated Franck–Condon envelopes, as using PBE0 (C_{2v} MnO_3) also predicted a broad unresolved spectrum like BPW91 [Fig. 2(a)], whereas using TPSSH predicted a resolved vibrational progression of four narrow bands, similar to B3LYP [Fig. 2(b)]. Comparison of the two differing simulations in Fig. 2 suggests that the Franck–Condon envelope for photodetachment to the ground state of MnO_3 with a D_{3h} geometry matches the direct detachment features of both our spectrum (black, Fig. 2) and the previously reported spectrum (red, Fig. 2) more closely than for a pyramidal MnO_3 , concluding that the neutral is in fact trigonal planar.¹

Our experiments provide additional information about the electronic structure of MnO_3^- through the PADs. The simple d-block model of transition metal complexes can be used to estimate the nature of high lying molecular orbitals (MOs).⁴ These will have a large contribution from the partially filled d-orbitals of the metal and are expected to have anti- or non-bonding character overall.⁴ For MnO_3^- , the metal-centred d_{xy} and $d_{x^2-y^2}$ orbitals on Mn will be raised in energy due to overlap with the oxygen s-orbitals and p-orbitals orientated along the internuclear axes forming MOs of σ^* character. The d_{xz} and d_{yz} orbitals will be raised somewhat in energy due to a π^* interaction with the remaining p-orbitals on the O atoms. The d_{z^2} orbital will be the lowest in energy and essentially non-bonding with the oxygen-centred orbitals. The resultant d-block picture is summarised in Fig. 3(a).

For comparison, the relevant MOs of MnO_3^- were also computed. The calculated highest occupied, lowest unoccupied and lowest unoccupied plus one molecular orbital (HOMO, LUMO, and LUMO+1, respectively) calculated at the B3LYP/aug-cc-pVTZ level of theory are shown in Fig. 3(b). The HOMO has predominantly d_{z^2} character, with a small contribution from MOs localised on the O atoms. The LUMO and LUMO+1 are essentially degenerate and consist mainly of contributions from the d_{xy} and d_{yz} localised on the Mn and p-orbitals localised on the O atoms. Therefore, the orbitals

predicted from electronic structure methods, from the d-block model, and from a symmetry-adapted linear-combination of atomic orbitals are all fully consistent.

Photoelectron imaging provides information about the nature of the high-lying occupied MOs via the PAD. According to Koopmans' theory, photodetachment would remove an electron from the HOMO [see Fig. 3(a)], which has predominantly d_{z^2} character. Ejection of an electron from this MO is expected to have predominantly p-wave character (partial waves of f-character will also contribute but are likely to have lower cross-sections based on centrifugal barriers), which would lead to a PAD characterised by a positive β_2 value.³⁷ This is consistent with the observed photoelectron image for MnO_3^- in Fig. 1(b). The excellent agreement between the experimental data, electronic structure calculations and simple d-block model, indicates the validity of the theoretical approaches, the value of the d-block model and the power of photoelectron imaging for understanding the electronic structure of transition metal complexes.

To conclude, comparison of the photoelectron spectrum of MnO_3^- to calculated Franck–Condon factors has allowed us to reassign the ground electronic state of MnO_3 to have a trigonal planar geometry as expected. The observed anisotropy for the photoelectron emission from MnO_3^- can be justified via a simple d-block model and verified by electronic structure calculations, both of which indicate that the HOMO has predominantly d_{z^2} character.

ACKNOWLEDGMENTS

Jemma Gibbard is grateful for the support of a Royal Society University Research Fellowship.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Jemma A. Gibbard: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Jonathan Reppel:** Formal analysis (equal); Investigation (equal). **Jan. R. R. Verlet:** Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available in Zenodo at <https://zenodo.org/record/8356163>.

REFERENCES

- G. L. Gutsev, B. K. Rao, P. Jena, X. Li, and L.-S. Wang, "Experimental and theoretical study of the photoelectron spectra of MnO_x^- ($x = 1-3$) clusters," *J. Chem. Phys.* **113**(4), 1473–1483 (2000).
- T. E. H. Walker and J. T. Waber, "Spin-orbit coupling photoionization," *J. Phys. B: At. Mol. Phys.* **7**(6), 674–692 (1974).
- P. Pyykko, "Relativistic effects in structural chemistry," *Chem. Rev.* **88**(3), 563–594 (1988).

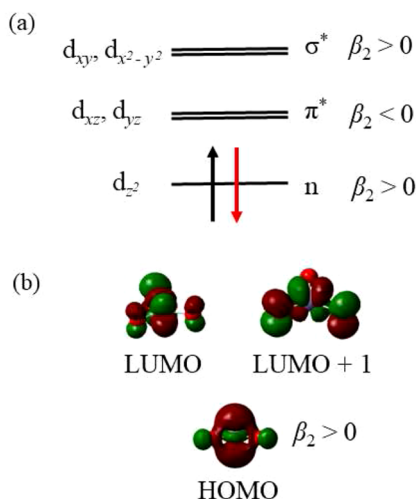


FIG. 3. The (a) d-block diagram and (b) the calculated HOMO, LUMO and LUMO+1 of MnO_3^- .

- ⁴Y. Jean, *Molecular Orbitals of Transition Metal Complexes* (Oxford University Press, Oxford, 2005).
- ⁵J. A. Gibbard and J. R. R. Verlet, "Photoelectron imaging of PtI_2^- and its PtI^- photodissociation product," *J. Chem. Phys.* **156**(13), 134303 (2022).
- ⁶J. Joseph, K. Pradhan, P. Jena, H. Wang, X. Zhang, Y. Jae Ko, and K. H. Bowen, Jr., "Evolution of superhalogen properties in PtCl_n clusters," *J. Chem. Phys.* **136**(19), 194305 (2012).
- ⁷R. Wesendrup and P. Schwerdtfeger, "Structure and electron affinity of platinum fluorides," *Inorg. Chem.* **40**(14), 3351–3354 (2001).
- ⁸J. A. Gibbard and J. R. R. Verlet, "Photoelectron imaging study of the diplatinum iodide dianions $[\text{Pt}_2\text{I}_6]^{2-}$ and $[\text{Pt}_2\text{I}_8]^{2-}$," *J. Phys. Chem. A* **126**(22), 3495–3501 (2022).
- ⁹J. B. Kim, M. L. Weichman, and D. M. Neumark, "Structural isomers of Ti_2O_4 and Zr_2O_4 anions identified by slow photoelectron velocity-map imaging spectroscopy," *J. Am. Chem. Soc.* **136**(19), 7159–7168 (2014).
- ¹⁰V. D. Moravec and C. C. Jarrold, "Study of the low-lying states of NiO^- and NiO using anion photoelectron spectroscopy," *J. Chem. Phys.* **108**(5), 1804–1810 (1998).
- ¹¹X.-B. Wang and L.-S. Wang, "Photodetachment of free hexahalogenometallate doubly charged anions in the gas phase: $[\text{ML}_6]^{2-}$, ($\text{M} = \text{Re}, \text{Os}, \text{Ir}, \text{Pt}$; $\text{L} = \text{Cl}$ and Br)," *J. Chem. Phys.* **111**(10), 4497–4509 (1999).
- ¹²P. Jäger, K. Brendle, U. Schwarz, M. Himmelsbach, M. K. Armbruster, K. Fink, P. Weis, and M. M. Kappes, "Q and Soret band photoexcitation of isolated palladium porphyrin tetraanions leads to delayed emission of nonthermal electrons over microsecond time scales," *J. Phys. Chem. Lett.* **7**(7), 1167–1172 (2016).
- ¹³A. Sanov, "Laboratory-frame photoelectron angular distributions in anion photodetachment: Insight into electronic structure and intermolecular interactions," *Annu. Rev. Phys. Chem.* **65**(1), 341–363 (2014).
- ¹⁴K. L. Reid, "Photoelectron angular distributions," *Annu. Rev. Phys. Chem.* **54**(1), 397–424 (2003).
- ¹⁵J. Cooper and R. N. Zare, "Angular distribution of photoelectrons," *J. Chem. Phys.* **48**(2), 942–943 (1968).
- ¹⁶B. F. Parsons, S. M. Sheehan, K. E. Kautzman, T. A. Yen, and D. M. Neumark, "Photoelectron imaging of I_2^- at 5.826 eV," *J. Chem. Phys.* **125**(24), 244301 (2006).
- ¹⁷J. Czekner, L. F. Cheung, and L.-S. Wang, "Probing the structures of neutral B_{11} and B_{12} using high-resolution photoelectron imaging of B_{11}^- and B_{12}^- ," *J. Phys. Chem. C* **121**(20), 10752–10759 (2017).
- ¹⁸J. L. Woodhouse, A. Henley, R. Lewin, J. M. Ward, H. C. Hailes, A. V. Bochenkova, and H. H. Fielding, "A photoelectron imaging study of the deprotonated GFP chromophore anion and RNA fluorescent tags," *Phys. Chem. Chem. Phys.* **23**(35), 19911–19922 (2021).
- ¹⁹A. V. Davis, R. Wester, A. E. Bragg, and D. M. Neumark, "Time-resolved photoelectron imaging of the photodissociation of I_2^- ," *J. Chem. Phys.* **118**(3), 999–1002 (2003).
- ²⁰X.-P. Xing, X.-B. Wang, and L.-S. Wang, "Photoelectron imaging of doubly charged anions, $^-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2^-$ ($n = 2-8$): Observation of near 0 eV electrons due to secondary dissociative autodetachment," *J. Phys. Chem. A* **114**(13), 4524–4530 (2010).
- ²¹J. L. Mason, H. Harb, A. Abou Taka, C. D. Huizenga, H. H. Corzo, H. P. Hratchian, and C. C. Jarrold, "New photoelectron–valence electron interactions evident in the photoelectron spectrum of Gd_2O^- ," *J. Phys. Chem. A* **125**(45), 9892–9903 (2021).
- ²²J. Lecointre, G. M. Roberts, D. A. Horke, and J. R. R. Verlet, "Ultrafast relaxation dynamics observed through time-resolved photoelectron angular distributions," *J. Phys. Chem. A* **114**(42), 11216–11224 (2010).
- ²³L. H. Stanley, C. S. Anstöter, and J. R. R. Verlet, "Resonances of the anthracenyl anion probed by frequency-resolved photoelectron imaging of collision-induced dissociated anthracene carboxylic acid," *Chem. Sci.* **8**(4), 3054–3061 (2017).
- ²⁴W. C. Wiley and I. H. McLaren, "Time-of-flight mass spectrometer with improved resolution," *Rev. Sci. Instrum.* **26**(12), 1150–1157 (1955).
- ²⁵G. M. Roberts, J. L. Nixon, J. Lecointre, E. Wrede, and J. R. R. Verlet, "Toward real-time charged-particle image reconstruction using polar onion-peeling," *Rev. Sci. Instrum.* **80**(5), 053104 (2009).
- ²⁶A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange," *J. Chem. Phys.* **98**(7), 5648–5652 (1993).
- ²⁷R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," *J. Chem. Phys.* **96**(9), 6796–6806 (1992).
- ²⁸J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, "Climbing the density functional ladder: Nonempirical meta-generalized gradient approximation designed for molecules and solids," *Phys. Rev. Lett.* **91**(14), 146401 (2003).
- ²⁹C. Adamo and V. Barone, "Toward reliable density functional methods without adjustable parameters: The PBE0 model," *J. Chem. Phys.* **110**(13), 6158–6170 (1999).
- ³⁰J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, "Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation," *Phys. Rev. B* **46**(11), 6671–6687 (1992).
- ³¹A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Phys. Rev. A* **38**(6), 3098–3100 (1988).
- ³²P. J. Hay, "Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms," *J. Chem. Phys.* **66**(10), 004377–4384 (2008).
- ³³A. J. H. Wachters, "Gaussian basis set for molecular wavefunctions containing third-row atoms," *J. Chem. Phys.* **52**(3), 1033–1036 (2003).
- ³⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.
- ³⁵B. Baguenard, J. C. Pinaré, C. Bordas, and M. Broyer, "Photoelectron imaging spectroscopy of small tungsten clusters: Direct observation of thermionic emission," *Phys. Rev. A* **63**(2), 023204 (2001).
- ³⁶B. Baguenard, J. C. Pinaré, F. Lépine, C. Bordas, and M. Broyer, "Thermionic emission in small carbon cluster anions," *Chem. Phys. Lett.* **352**(3–4), 147–153 (2002).
- ³⁷E. P. Wigner, "On the behavior of cross sections near thresholds," *Phys. Rev.* **73**(9), 1002–1009 (1948).