

COMMENTS

Comment on “A New Proposal for the Ground State of the FeO⁻ Cluster in the Gas Phase and for the Assignment of Its Photoelectron Spectra”Daniel M. Neumark^{*,†} and W. Carl Lineberger[‡]

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In “A New Proposal for the Ground State of the FeO⁻ Cluster ...” by Hendrickx and Anam,¹ the authors attempt to interpret the photoelectron spectrum of FeO⁻ by proposing that the ground state of FeO⁻ is not a ⁴Δ state, the currently accepted assignment, but instead is a ⁶Σ⁺ state. The photoelectron spectrum^{2,3} of FeO⁻ is complex, given that the ground electronic state of neutral FeO is a ⁵Δ state.⁴ However, the proposed reassignment of the anion ground state is clearly incorrect and appears to be based on an incomplete and highly selective reading of the experimental data on this system. The key issues are summarized below.

First, this proposed assignment cannot be reconciled with the very high resolution (~0.001 cm⁻¹) autodetachment spectrum of FeO⁻ reported by Andersen et al.⁵ This paper, which was inexplicably not referenced by Hendrickx, presents fully rotationally resolved electronic spectra of FeO⁻ that originate from a ground state with the spin-orbit fine structure characteristic of a ⁴Δ state; specifically, bands originating from the Ω = 7/2, 5/2, and 3/2 spin-orbit components with an average spacing of 233 cm⁻¹ were identified. None of this fine structure would have been seen from a ⁶Σ⁺ state, which should be a Hund's case (b) molecule with no spin-orbit splitting. Moreover, the experimental rotational constant of 0.4972 cm⁻¹ for the Ω =

7/2 multiplet yields a bond length of 1.641 Å, in good agreement with the bond length of 1.635 Å calculated by Hendrickx for the ⁴Δ state of FeO⁻, but in poorer agreement with the bond length of 1.683 Å calculated for the ⁶Σ⁺ state.

Second, the zero-electron-kinetic-energy (ZEKE) spectrum of FeO⁻ measured by Drechsler et al.,⁶ which was referenced by Hendrickx, exhibits partial rotational resolution on the origin band that was indeed fit very well using the rotational constants from Andersen et al., with an overall band contour consistent with detachment from a ⁴Δ anion state. In addition, the ZEKE spectrum exhibited spin-orbit fine structure that was shown to be fully consistent with the ⁴Δ spin-orbit splittings of Andersen et al. Neither the rotational structure nor fine structure in the ZEKE spectrum is consistent with a ⁶Σ⁺ ground state for the anion.

Finally, we concur with Hendrickx and Anam that the photoelectron spectrum of FeO⁻ is not fully understood. At low electron binding energy, it is dominated by transitions to the ⁵Δ ground state of FeO but also exhibits minor transitions that have been tentatively assigned⁶ to an excited ⁷Σ⁺ excited state of FeO. This state is not accessible by one-electron detachment from the anion ⁴Δ state. However, while the ⁷Σ⁺ state is accessible by one-electron detachment from the proposed anion ⁶Σ⁺ ground state, the ⁵Δ state, which is responsible for most of the transitions in this region, is not (as pointed out by Hendrickx). Thus, even leaving out the issues considered in the preceding paragraphs, the proposed reassignment of the FeO⁻ ground state is perplexing, as it appears to cause more problems than it solves.

References and Notes

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