

# NRC Publications Archive Archives des publications du CNRC

# Far-IR spectra and structures of small cationic ruthenium clusters : evidence for cubic motifs

Kerpal, Christian; Harding, Dan J.; Rayner, David M.; Lyon, Jonathan T.; Fielicke, André

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

# Publisher's version / Version de l'éditeur:

https://doi.org/10.1021/jp510471k The Journal of Physical Chemistry C, 119, 20, pp. 10869-10875, 2015-01-05

# NRC Publications Record / Notice d'Archives des publications de CNRC:

https://nrc-publications.canada.ca/eng/view/object/?id=0f5a9b5b-c1a7-46b4-9345-7e97f15ffc33 https://publications-cnrc.canada.ca/fra/voir/objet/?id=0f5a9b5b-c1a7-46b4-9345-7e97f15ffc33

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at <u>https://nrc-publications.canada.ca/eng/copyright</u> READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site https://publications-cnrc.canada.ca/fra/droits LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

**Questions?** Contact the NRC Publications Archive team at PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





# Far-IR Spectra and Structures of Small Cationic Ruthenium Clusters: Evidence for Cubic Motifs

Christian Kerpal,<sup>†,⊥</sup> Dan J. Harding,<sup>†,#</sup> David M. Rayner,<sup>‡</sup> Jonathan T. Lyon,<sup>§</sup> and André Fielicke<sup>\*,†,∥</sup>

<sup>†</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

<sup>‡</sup>National Research Council, 100 Sussex Drive, Ottawa, Ontario K1A OR6, Canada

<sup>§</sup>Department of Natural Sciences, Clayton State University, Morrow, Georgia 30260, United States

<sup>II</sup>Institut für Optik und Atomare Physik, Technische Universität Berlin, 10623 Berlin, Germany

**Supporting Information** 

**ABSTRACT:** Far-IR vibrational spectra of small ruthenium cluster cations  $(Ru_7^+, Ru_8^+, and Ru_9^+)$  are measured via infrared multiple photon dissociation (IR-MPD) spectroscopy using Ar atoms as messenger for the absorption. These spectra are compared to results from density functional theory calculations, leading to structural assignments. The pure functional PBE leads to better agreement with the experimental data compared to the hybrid functional PBE0. For all three cluster sizes the structures assigned are based on a cubic motif and are a distorted cube missing one corner atom  $(Ru_7^+)$ , a slightly distorted cube  $(Ru_8^+)$ , and a face-capped cube  $(Ru_9^+)$ .



### INTRODUCTION

Ruthenium shows interesting catalytic properties for a number of industrially relevant applications including CO oxidation<sup>1</sup> and ammonia synthesis.<sup>2,3</sup> In particular, the latter has attracted much attention due to ruthenium's activity at significantly lower temperatures than traditional Haber–Bosch synthesis. Consequently, carbon-supported ruthenium is now industrially used as a catalyst in the low-pressure ammonia synthesis of Kellogg, Brown, and Root (KBR Advanced Ammonia Process).<sup>4</sup> As for many catalyzed reactions, however, the exact details of the reaction mechanism remain unclear and a high structure sensitivity of the process has been found.<sup>3,5–7</sup>

To exploit ruthenium's full potential as a catalyst, a significantly better understanding of its physical and chemical properties is necessary, specifically given its high material cost. One way of potentially getting deeper insights on an atomic or molecular level is using gas-phase Ru clusters as model systems to reveal fundamental aspects of the chemical and physical behavior of dispersed catalysts. Unfortunately, only a limited number of such studies exist. They include one investigating the magnetic properties of neutral Ru clusters that suggested the magnetic properties of neutral Ku clusters that  $\sigma_{BB}$  because they have low magnetic moments.<sup>8</sup> Two other studies have used infrared multiple photon dissociation (IR-MPD) spectroscopy to investigate the binding of CO and N<sub>2</sub> to charged and neutral Ru<sub>n</sub> clusters, respectively.<sup>9,10</sup> A recent study has investigated the reactivity of  $\operatorname{Ru}_n^+$  clusters (n = 2-6) with ligands such as CO, CO2, CD4, N2, and D2 and reactions leading to CO methanation using ion-trap mass spectrometry.<sup>11</sup> Finally, medium sized anionic  $\operatorname{Ru}_n^-$  clusters (n = 19, 28, 38, 44) have been investigated using trapped ion electron diffraction (TIED) showing their structures to be based on octahedral motifs.<sup>12</sup> More recently this study has been extended also to smaller anionic Ru clusters including  ${\rm Ru_8^-}$  and  ${\rm Ru_9^-},$  revealing that they are based on cubic structures.  $^{13}$ 

In contrast, a number of theoretical studies have been published on Ru clusters (see refs 14-21 and references therein). Unfortunately, the results are inconclusive as the favored structures are very sensitive to the level of theory and calculation details. Within density functional theory (DFT), for example, very different results can be obtained depending on the exchange-correlation functional used, a problem often ascribed to the presence of numerous low-lying excited states due to the open 4d shells in Ru with which DFT is known to struggle. It was found that functionals using the generalgradient approximation (GGA) favor square or cubic structures,<sup>18</sup> whereas calculations using the hybrid functional PBE0 showed different structures and lead to a better agreement with high-level calculations for Ru<sub>2</sub> and Ru<sub>3</sub>.<sup>16</sup> Interestingly, the case of rhodium clusters is similar in that GGA functionals favor square and cubic structures, whereas a combined IR-MPD and computational study showed Rh<sub>8</sub><sup>+</sup> to have a noncubic structure as correctly described by hybrid functionals.<sup>22</sup> Notably, such unusual cube-based structures have also been predicted for clusters of osmium and iridium, 23-28 the heavier homologues of ruthenium and rhodium in the periodic table.

To contribute to solving this puzzle and to establish reference structures for further studies we have measured the

Special Issue: Current Trends in Clusters and Nanoparticles Conference

Received:October 17, 2014Revised:December 17, 2014Published:January 5, 2015

vibrational spectra of gas-phase  $\operatorname{Ru}_n^+$  (n = 7-9) clusters with far-IR-MPD spectroscopy<sup>29</sup> in the frequency range of 120 to 325 cm<sup>-1</sup> using weakly bound Ar atoms as messengers for the IR absorption. We then compare these far-infrared spectra with the results of DFT based calculations to obtain structural information.

## EXPERIMENTAL AND THEORETICAL METHODS

The experiments were carried out employing a pulsed molecular beam setup connected to the beamline of the Free Electron Laser for Infrared eXperiments (FELIX)<sup>30</sup> in The Netherlands as the far-IR light source. Both the experimental setup and the data analysis procedure have been described in more detail elsewhere.<sup>29,31</sup> Briefly, a plasma is formed by pulsed laser ablation from a rotating Ru rod. The clusters are formed by quenching the plasma with a gas pulse comprising 0.2% argon in helium. The clusters are carried by the gas through a copper channel cooled to about 170 K where the Ru<sub>n</sub>Ar<sub>m</sub><sup>+</sup> complexes are produced. A molecular beam is formed by expansion into vacuum. The beam passes first a skimmer and then an aperture of 1 mm diameter before entering the extraction region of a time-of-flight mass spectrometer with which the mass distribution is analyzed. The FELIX beam counter propagates along the molecular beam. It is weakly focused through the aperture and runs at half the rate of the ablation laser so that mass distributions with and without IR irradiation are recorded alternately. If the IR radiation is resonant with one of the internal vibrational modes of the cluster (complex), one or several IR photons can be sequentially absorbed and the resulting heating can eventually lead to dissociation of the argon complex. Depletion spectra are obtained by scanning the IR light frequency and measuring the ratio of the signal intensities in the mass distributions with and without IR irradiation. This is then converted into cross sections and normalized by the photon fluence to obtain the IR spectra shown here, which show the raw data together with a binomially weighted seven point average.

The amount of argon used was sufficient to produce  $Ru_7Ar^+$ ,  $Ru_8Ar^+$ , and  $Ru_9Ar^+$  complexes but also resulted in significant amounts of  $Ru_7Ar_2^+$  and  $Ru_8Ar_2^+$  complexes being formed. The IR-MPD spectra of  $Ru_7Ar^+$  and  $Ru_8Ar^+$  are affected by the depletion of the respective diargon complexes into their mass channels. As the spectra of the  $Ru_nAr_2^+$  (n = 7,8) complexes are sufficiently similar to their monoargon counterparts we can conclude only a minor influence of the messenger atom(s), and we analyze the spectra of the undisturbed  $Ru_nAr_2^+$  complexes (the spectra of the mono-argon complexes are shown in Figure S1 in the Supporting Information).

The DFT calculations presented here were performed using the TURBOMOLE V6.5 program package<sup>32</sup> and utilize the resolution of the identity (RI) approximation. Two different sets of functionals, basis sets, and electronic core potentials have been employed, namely, PBE with def2-TZVP and def2ecp and PBE0 with def-TZVP and def-ecp.<sup>33–36</sup> These choices were made to account for the different results obtained for ruthenium (and rhodium) clusters when using hybrid and nonhybrid functionals and to allow for comparison between them. The starting structures to be optimized were generated both on the basis of structures known for other transition metal clusters and also using a basin hopping algorithm as described in detail elsewhere.<sup>37</sup> Different basin hopping runs were performed for both a number of selected fixed spin states and using Fermi level smearing, to allow the spin state to change. In the optimizations, no symmetry constraints were used, and the symmetries given below are the approximate symmetries of the final geometries. The only exception is  $Ru_8^+$  calculated using the PBE functional, see below. For many structures the energies of different spin multiplicities (2S + 1) are competitive in energy, and especially for the hybrid functional, high spin states have to be considered to find the minimum energy state for a structural motif. The tested structures are fully relaxed, and the vibrational spectra were calculated using the harmonic oscillator approximation. The vibrational frequencies resulting from the PBE calculations were scaled by a factor of 0.966. In contrast to rhodium, calculations using the nonhybrid PBE functional give, compared to PBE0, better agreement with the experimental data and will be shown primarily.

### RESULTS

 $Ru_7^+$ . The experimental IR-MPD spectrum of  $Ru_7Ar_2^+$  is shown in Figure 1 together with the vibrational spectra and relative energies of several structural isomers calculated at the PBE/def2-TZVP level. For each structure, only the isomer corresponding to the lowest energy state is shown (for the dependence of relative energy and IR spectra on the number of unpaired electrons, see Figures S2 and S3 in the Supporting Information). For many structural motifs two or more spin



**Figure 1.** IR-MPD spectrum of  $Ru_7Ar_2^+$  and vibrational spectra for isomers of  $Ru_7^+$  corresponding to the lowest energy spin states for different structural motifs (PBE/def2-TZVP). All calculated spectra are folded with a Gaussian line width function of 7 cm<sup>-1</sup> full width at half-maximum for ease of comparison to the experimental data.

## The Journal of Physical Chemistry C

states are competitive in energy, representing low lying excited states. It shall be noted that the comparison is between the calculated spectra of the bare clusters and the IR-MPD spectrum of the Ar complex. However, earlier investigations on transition metal clusters showed that the binding of Ar atoms in most cases have some effect on the IR intensities, while the vibrational frequencies usually shift only little.<sup>38,39</sup>

The best match to the experimental spectrum is provided by the calculated spectrum of 7b in a singlet state, matching the number and approximate position of the experimentally observed peaks and to some extent also their relative intensities. The structure of isomer 7b is a distorted cube with one missing edge atom, an unusual structure when compared to those of other 7-atom transition metal clusters, which usually prefer closer packing and often have pentagonal bipyramidal structures.<sup>40-44</sup> This structure can also be described as a facecapped trigonal prism, and the structures of the four most stable structural isomers (7a-7d) can be related to such a motif. The spectrum of the calculated lowest energy isomer 7a (S = 3/2) matches the experiment clearly worse, despite its structure being very similar to that of 7b. This similarity also explains why for some higher spin states (including the shown case of three unpaired electrons) 7b collapses into 7a during optimization. Interestingly, the other low lying structural isomers prefer higher spin states and are all significantly higher in energy (at least 0.5 eV) than 7a (S = 3/2) and 7b (S = 1/2), which are essentially isoenergetic. In comparison, calculations using the PBE0 hybrid functional predict two distorted pentagonal bipyramids as lowest energy isomers, having 19 and 21 unpaired electrons. Such high spin states are at odds with the low (or absent) magnetic moments determined for small neutral Ru clusters,<sup>8</sup> and also their calculated vibrational spectra do not match the experiment well (Figure S4 in Supporting Information). These bipyramidal structures are similar to those found as lowest energy isomers for Rh7<sup>+</sup> when using both PBE and PBE0.42

 $Ru_8^+$ . The case of  $Ru_8^+$  is particularly interesting as calculations with both PBE and PBE0 functionals predict low-spin, low-energy, cubic isomers that provide acceptable matches of their calculated vibrational spectrum with the experiment (see below). Again, the results using the PBE functional are discussed first as they match the experiment best and are shown together with the IR-MPD spectrum of  $Ru_8Ar_2^+$ in Figure 2. The lowest energy isomers, 8a (S = 3/2) and 8a\* (S = 3/2), are slightly distorted cubes (see Figure 3) and are basically isoenergetic. Isomer 8a (S = 3/2) is an axially stretched cube of  $D_{4h}$  symmetry, where four edges have lengths of 2.36 Å, while the other edges are 2.29 Å long. Isomer 8a\* (S = 3/2) is of  $D_{2d}$  symmetry and is essentially, opposite to 8a, a compressed cube with slight distortions in the top and base faces and four bonds with lengths of 2.30, 2.31, and 2.34 Å, respectively. The electronic structure in terms of occupation and symmetry of the frontier orbitals of both cubic structures is very similar and differs only slightly, see Figure 3. Inspection of the character of the partially occupied orbitals reveals that this corresponds to a Jahn-Teller-type distortion from  $O_h$ symmetry.

Isomer  $8a^*$  (S = 3/2) has a vibrational spectrum that fits the experiment well, whereas isomer 8a shows one single intense band that matches one of the intense features in the experimental spectrum. The notable difference in the calculated vibrational spectra of isomers 8a and  $8a^*$  is surprising in the first place but becomes clear when considering the high





Figure 2. IR-MPD spectrum of  $Ru_8Ar_2^+$  together with the calculated vibrational spectra, energies, structural motifs, and spin-dependent relative energies of several calculated low-lying isomers (PBE/def2-TZVP).

symmetry of isomer 8a leading to degenerate vibrational levels and many IR inactive modes. In the probed cluster complexes this high symmetry will be broken by the addition of argon atoms, and thus, the vibrational spectra of the respective argon complexes of isomers 8a and 8a\* might change. Given the good match between the calculated spectrum of the lower symmetry isomer 8a\* and the experiment, an assignment to a cubic structural motif is still very likely, specifically when compared to other potential structural motifs (see below). It is, however, not clear if two (or more) (Jahn-Teller) distorted isomers exist in the beam or if just one isomer is present. The next low-lying isomers are already significantly higher in energy (at least 1.8 eV) and their calculated vibrational spectra clearly provide poorer matches to the experiment. Among them is a rhombic prism 8b (S = 1/2) and a more distorted version thereof, 8c (S = 7/2). A distorted bicapped octahedron that has been found as the ground state structure for Rh<sub>8</sub><sup>+</sup> (using PBE0)<sup>22,42</sup> is clearly not favored here, as it is nearly 3 eV higher in energy compared to the putative ground state.

The bicapped octahedral structure is, however, favored even for ruthenium when using the PBE0 hybrid functional instead of PBE (see Figure 4). There, the two lowest energy isomers **8d-0** (S = 23/2) and **8d\*-0** (S = 25/2) have such a structure. Both have high spin states, and the lowest energy isomer is favored over the most stable cubic isomer by 0.35 eV. The nearly isoenergetic cubic isomers **8a-0** (S = 1/2) and **8a\*-0** (S = 1/2) have only one unpaired electron each and are slightly differently distorted cubes, as in the case of the cubic structures identified in the PBE calculations. The best match to the experiment is provided by the calculated vibrational spectrum of **8a\*-0** (S = 1/2) when applying a scaling factor of about 0.95.



**Figure 3.** Comparison of the geometries (distortions are strongly exaggerated) and the electronic structures of the two cubic low energy isomers of  $Ru_8^+$  **8a** (left) and **8a**\* (right) predicted at the PBE/def2-TZVP level of theory. For the quartet states the three singly occupied molecular orbitals (SOMOs) and the four next unoccupied orbitals are shown (majority spins). Fully occupied lower energy MOs show nearly the same shapes and ordering for both structures, and only two selected totally symmetric MOs are shown.

The spectrum of the calculated ground-state in PBE0, **8d-0** (S = 23/2), provides a poorer match specifically in terms of the peak spacing. Overall, neither the cubic nor octahedral motif yield a vibrational match as good as that provided by the calculations using the PBE functional, and again, like in the case of Ru<sub>7</sub><sup>+</sup>, PBE0 predicts close packed high spin state motifs to be the lowest in energy.

**Ru**<sub>9</sub><sup>+</sup>. Ru<sub>9</sub>Ar<sup>+</sup> is the largest cluster size for which an IR-MPD spectrum has been obtained. A comparison of its experimental spectrum with the IR spectra of different isomers calculated using PBE is presented in Figure 5. Clearly the best match to the experimental spectrum is provided by the calculated vibrational spectrum of isomer 9a (S = 7/2), which is a face capped cube, and the calculated lowest energy isomer. The second lowest isomer 9b (S = 3/2) lies close in energy (+0.12 eV) and is an edge capped cube. Its calculated vibrational spectrum does not match the experiment as well. The next lowest energy isomers are significantly higher in energy and, with the exception of 9e (S = 3/2), if one ignores the very low frequency band at 140 cm<sup>-1</sup>, provide poor matches to the experiment. Isomers 9c and 9e are differently capped rhombic



**Figure 4.** Experimental IR-MPD spectrum of  $Ru_8Ar_2^+$  and calculated lowest energy structures and vibrational spectra for  $Ru_8^+$  using the PBE0 hybrid functional.

prisms, and **9e** resembles **9a** but shows a significant distortion of the cubic base. Isomer **9d** is a triply face-capped trigonal prism representing the lowest energy structure found for  $Rh_9^+$  (the vibrational spectrum cannot, however, explain the experimental IR-MPD spectrum there).<sup>42</sup>

The PBE0 calculations give a clearly different picture. They find structures that can be described as either distorted tricapped trigonal prisms or capped anticubes as lowest energy isomers. The ground state is a tricapped trigonal prism with 27 unpaired electrons and has a calculated vibrational spectrum that fits the experimental spectrum acceptably (see Supporting Information). Given the earlier mentioned findings on the low magnetic moments of larger Ru<sub>n</sub> clusters<sup>8</sup> and even more importantly those on the structure of the anionic Ru<sub>8</sub><sup>-</sup> and Ru<sub>9</sub><sup>-</sup> clusters determined using TIED,<sup>13</sup> a cubic structure as predicted by PBE still seems more likely, especially as it is consistent with the good description achieved for Ru<sub>7</sub><sup>+</sup> and Ru<sub>8</sub><sup>+</sup>, too.

#### DISCUSSION

The IR-MPD spectra for all three presented cluster sizes can be consistently explained by calculated vibrational spectra of relatively low-spin, low(est)-energy structures based on cubic motifs, using the pure DFT functional PBE. This assignment of low-spin structures is also consistent with other experimental findings. Magnetic deflection experiments on larger neutral ruthenium clusters (n = 10-105) find them to be nonmagnetic ( $\mu_{expt} = 0.000 \pm 0.004 \ \mu_{B}/atom$ ), or in case of super-paramagnetism give an upper limit of 0.35  $\mu_{B}/atom$ .<sup>8</sup> Greater support is offered by recent investigations of anionic Ru<sub>8</sub><sup>-</sup> and



**Figure 5.** IR-MPD spectrum of Ru<sub>9</sub>Ar<sup>+</sup> together with the calculated vibrational spectra on the def2-TZVP/PBE level for different isomers. In addition to the calculated spectrum of the putative ground state, the lowest energy spin states for other structural motifs are included.

 $Ru_{9}^{-}$  (as well as larger sizes) using trapped ion electron (TIED) diffraction that clearly identify cubic structural motifs.<sup>13</sup> The structures determined for the anionic clusters are very similar to those we find for the cations: Ru<sub>8</sub><sup>-</sup> is assigned to be a cube, slightly distorted toward D<sub>4h</sub> symmetry, and Ru<sub>9</sub><sup>-</sup> is a facecapped cube. While no TIED data for smaller clusters are available, structures for Ru<sub>4</sub><sup>-</sup>-Ru<sub>7</sub><sup>-</sup> have been predicted using the same theoretical methodology as used for the interpretation of the diffraction data (TPSS/def2-SVP) yielding, for instance, for Ru7<sup>-</sup> a defective cube structure,<sup>13</sup> similar to that found for Ru7<sup>+</sup>. Interestingly, the difference between the number of unpaired electrons predicted for the anionic clusters Ru<sub>8</sub>, Ru<sub>9</sub><sup>-</sup>, and their cationic counterparts is exactly two, just equal to the number of added electrons to change from a cation to an anion. This points to very fundamental similarities in the electronic structures of these species.

Together, this strongly indicates that, in contrast to the case of rhodium, ruthenium clusters in the investigated size range are better described using a pure DFT functional like PBE as compared to a hybrid functional such as PBE0. It also gives sufficient confidence that their structural motifs are indeed based on cubes, being very unusual for small transition metal clusters that usually favor polytetrahedral structures.<sup>40–44</sup> Given that rhodium and ruthenium are neighboring elements in the periodic table, the difference in both the preferred structural motifs and the suitable theoretical method to describe them is somewhat surprising. It probably shows again the difficulties of DFT in general to describe the open d-shell transition metal clusters, specifically when many low-lying electronic states are present, as indicated by the calculations using both pure DFT and hybrid methods. In that regard, the pure DFT functional might give the right answer for the wrong reason. It is equally possible, however, that the results are indeed extremely sensitive on the amount of Hartree–Fock included and that the 25% included in PBE0 is simply too large, leading to an overstabilization of the high-spin noncubic motifs.

Finally the question remains, to what particular binding interaction leads to a stabilization of the cubic structures? It has been suggested to be caused by "8-center bonds" at the example of  $Rh_8^{45}$  or by the overlap of orthogonal d-orbitals (in  $Ru_{12}$ ).<sup>20</sup> While these cationic ruthenium clusters contain occupied bonding molecular orbitals that resemble the previously proposed multiatom bonds, it is not clear how much these orbitals may stabilize cubic structures of transition metals. In particular, the totally symmetric lowest energy valence orbital (HOMO - 32) as shown in Figure 3 has been proposed to be indicative of 8-center bonding. We, however, find similar orbitals, essentially composed of an "in-phase" combination of  $d_{z^2}$  atomic orbitals, as lowest energy valence orbitals for  $Ru_7^+$ -Ru9<sup>+</sup> in various structures, cubic and noncubic ones, and even for clusters of different transition metals that clearly do not show cubic growth, like Nb<sub>8</sub>.<sup>41</sup>

#### CONCLUSIONS

The experimental IR-MPD spectra for Ru<sub>7</sub>Ar<sub>2</sub><sup>+</sup>, Ru<sub>8</sub>Ar<sub>2</sub><sup>+</sup>, and Ru<sub>9</sub>Ar<sup>+</sup> have been obtained and, by comparison with results from DFT calculations, cubic structures are assigned for all three cluster sizes. It is found that these ruthenium clusters are better described by the pure DFT functional PBE as compared to its hybrid counterpart PBE0 leading to more favorable agreement of the IR spectra for cubic isomers and a clear trend toward lower spin states. These findings are different from those for the clusters of rhodium, an element for which cubic cluster structures have also been predicted. The assigned isomers are in agreement with the results of magnetic deflection and trapped ion electron diffraction data on neutral and anionic clusters, respectively. The reason for this unusual behavior is unclear but has been suggested to be caused by the overlap of orthogonal d-orbitals.<sup>20°</sup> The question of why pure DFT functionals perform well for ruthenium clusters but only hybrid ones describe rhodium correctly is still unsolved, but our comparative experimental and theoretical study will hopefully serve as a basis for further studies to resolve this problem and to answer the question as to how reliably 4d transition metal clusters can be described by DFT methods.

## ASSOCIATED CONTENT

#### **S** Supporting Information

Comparison of the IR-MPD spectra of  $Ru_7Ar_{1,2}^+$  and  $Ru_8Ar_{1,2}^+$ , relative energies of the different structural isomers of  $Ru_7^+$ ,  $Ru_8^+$ , and  $Ru_9^+$  as a function of the number of unpaired electrons (2S) at the PBE/def2-TZVP level of theory, calculated IR spectra for the three lowest structural isomers of  $Ru_7^+$  as a function of spin multiplicity calculated at the PBE/ def2-TZVP level, and spectra of low-energy isomers at the PBE0/def-TZVP level. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: fielicke@physik.tu-berlin.de.

#### The Journal of Physical Chemistry C

#### Present Addresses

<sup>⊥</sup>Inorganic Chemistry Laboratory, South Parks Road, University of Oxford, OX1 3QR Oxford, United Kingdom.

<sup>#</sup>Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstraße 6, D-37077 Göttingen, Germany. Department of Dynamics at Surfaces, Max-Planck-Institut für Biophysikalische Chemie, Am Faßberg 11, D-37077 Göttingen, Germany.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Stichting voor Fundamental Onderzoek der Materie (FOM) for providing FELIX beamtime and thank the FELIX staff, particularly Dr. A.F.G (Lex) van der Meer and Dr. Britta Redlich, for their skillful assistance. We thank Gerard Meijer for his continued support. This work is supported by the Max Planck Society, the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technical University Berlin and funded by the Deutsche Forschungsgemeinschaft (DFG) and through the DFG research grant FI 893/3. Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research. D.J.H. thanks the Alexander von Humboldt Foundation for a fellowship. We are grateful to Dr. Detlef Schooss for communicating unpublished results on anionic Ru clusters.

#### REFERENCES

(1) Blume, R.; Havecker, M.; Zafeiratos, S.; Teschner, D.; Kleimenov, E.; Knop-Gericke, A.; Schlogl, R.; Barinov, A.; Dudin, P.; Kiskinova, M. Catalytically active states of Ru(0001) catalyst in CO oxidation reaction. *J. Catal.* **2006**, 239–361, 354.

(2) Logadottir, A.; Rod, T. H.; Norskov, J. K.; Hammer, B.; Dahl, S.; Jacobsen, C. J. H. The Bronsted-Evans-Polanyi relation and the volcano plot for ammonia synthesis over transition metal catalysts. *J. Catal.* **2001**, *197*, 229–231.

(3) Jacobsen, C. J. H.; Dahl, S.; Hansen, P. L.; Tornqvist, E.; Jensen, L.; Topsoe, H.; Prip, D. V.; Moenshaug, P. B.; Chorkendorff, I. Structure sensitivity of supported ruthenium catalysts for ammonia synthesis. *J. Mol. Catal. A* **2000**, *163*, 19–26.

(4) Bielawa, H.; Hinrichsen, O.; Birkner, A.; Muhler, M. The ammonia-synthesis catalyst of the next generation: Barium-promoted oxide-supported ruthenium. *Angew. Chem., Int. Ed.* **2001**, *40*, 1061–1063.

(5) Logadottir, A.; Norskov, J. K. Ammonia synthesis over a Ru(0001) surface studied by density functional calculations. *J. Catal.* **2003**, *220*, 273–279.

(6) Shetty, S.; Jansen, A. P. J.; van Santen, R. A. Active sites for N<sub>2</sub> dissociation on ruthenium. *J. Phys. Chem. C* **2008**, *112*, 17768–17771.

(7) Hansen, T. W.; Hansen, P. L.; Dahl, S.; Jacobsen, C. J. H. Support effect and active sites on promoted ruthenium catalysts for ammonia synthesis. *Catal. Lett.* **2002**, *84*, 7–12.

(8) Cox, A. J.; Louderback, J. G.; Apsel, S. E.; Bloomfield, L. A. Magnetism in 4D-transition metal-clusters. *Phys. Rev. B* 1994, 49, 12295–12298.

(9) Lyon, J. T.; Gruene, P.; Fielicke, A.; Meijer, G.; Rayner, D. M. Probing C-O bond activation on gas-phase transition metal clusters: Infrared multiple photon dissociation spectroscopy of Fe, Ru, Re, and W cluster CO complexes. *J. Chem. Phys.* **2009**, *131*, 184706.

(10) Kerpal, C.; Harding, D. J.; Lyon, J. T.; Meijer, G.; Fielicke, A. N<sub>2</sub> activation by neutral ruthenium clusters. *J. Phys. Chem. C* 2013, 117, 12153–12158.

(11) Lang, S. M.; Bernhardt, T. M.; Krstic, M.; Bonacic-Koutecky, V. The origin of the selectivity and activity of ruthenium-cluster catalysts for fuel-cell feed-gas purification: a gas-phase approach. Angew. Chem., Int. Ed. 2014, 53, 5467-5471.

(12) Waldt, E.; Ahlrichs, R.; Kappes, M. M.; Schooss, D. Structures of medium-sized ruthenium clusters: the octahedral motif. *ChemPhys-Chem* **2014**, *15*, 862–865.

(13) Waldt, E.; Hehn, A.-S.; Ahlrichs, R.; Kappes, M. M.; Schooss, D. Structural evolution of small ruthenium cluster anions. *J. Chem. Phys.* DOI: 10.1063/1.4905267.

(14) Kaiming, D.; Jinlong, Y.; Chuanyun, X.; Kelin, W. Electronic properties and magnetism of ruthenium clusters. *Phys. Rev. B* **1996**, *54*, 2191–2197.

(15) Zhang, W.; Zhao, H.; Wang, L. The simple cubic structure of ruthenium clusters. J. Phys. Chem. B 2004, 108, 2140-2147.

(16) Wang, L. L.; Johnson, D. D. Removing critical errors for DFT applications to transition-metal nanoclusters: Correct ground-state structures of Ru clusters. *J. Phys. Chem. B* **2005**, *109*, 23113–23117.

(17) Bae, Y.-C.; Osanai, H.; Kumar, V.; Kawazoe, Y. Atomic structures and magnetic behavior of small ruthenium clusters. *Mater. Trans.* **2005**, *46*, 159–162.

(18) Li, S. F.; Li, H. S.; Liu, J.; Xue, X. L.; Tian, Y. T.; He, H.; Jia, Y. Structural and electronic properties of  $Ru_n$  clusters (n = 2-14) studied by first-principles calculations. *Phys. Rev. B* **2007**, *76*, 045410.

(19) Aguilera-Granja, F.; Balbas, L. C.; Vega, A. Study of the structural and electronic properties of  $Rh_N$  and  $Ru_N$  clusters (N < 20) within the density functional theory. *J. Phys. Chem. A* **2009**, *113*, 13483–13491.

(20) Shetty, S.; Jansen, A. P. J.; van Santen, R. A. Magnetic, bonding and structural behavior of  $Ru_{12}$  and  $Ru_{13}$  clusters: Is  $Ru_{12}$  magic? *J. Mol. Struct.* **2010**, *954*, 109–114.

(21) Rösch, N.; Petrova, G. P.; Petkov, P. S.; Genest, A.; Kruger, S.; Aleksandrov, H. A.; Vayssilov, G. N. Impurity atoms on small transition metal clusters. Insights from density functional model studies. *Top. Catal.* **2011**, *54*, 363–377.

(22) Harding, D. J.; Walsh, T. R.; Hamilton, S. M.; Hopkins, W. S.; Mackenzie, S. R.; Gruene, P.; Haertelt, M.; Meijer, G.; Fielicke, A. Communications: The structure of  $Rh_8^+$  in the gas phase. *J. Chem. Phys.* **2010**, *132*, 011101.

(23) Takahashi, K.; Isobe, S.; Ohnuki, S. The structural and electronic properties of small osmium clusters (2-14): A density functional theory study. *Chem. Phys. Lett.* **2013**, 555, 26–30.

(24) Du, J.; Sun, X.; Chen, J.; Jiang, G. A theoretical study on small iridium clusters: structural evolution, electronic and magnetic properties, and reactivity predictors. *J. Phys. Chem. A* **2010**, *114*, 12825–12833.

(25) Zhang, W.; Xiao, L.; Hirata, Y.; Pawluk, T.; Wang, L. The simple cubic structure of Ir clusters and the element effect on cluster structures. *Chem. Phys. Lett.* **2004**, 383, 67–71.

(26) Chen, M.; Dixon, D. A. Low-lying electronic states of  $Ir_n$  clusters with n = 2-8 predicted at the DFT, CASSCF, and CCSD(T) levels. *J. Phys. Chem. A* **2013**, *117*, 3676–3688.

(27) Guo, P.; Zheng, J.-M.; Zhao, P.; Zheng, L.-L.; Ren, Z.-Y. The relativistic density functional investigations on geometries, electronic and magnetic properties of  $Ir_n$  (n = 1–13) clusters. *Chin. Phys. B* **2010**, *19*, 083601.

(28) Feng, J.-N.; Huang, X.-R.; Li, Z.-S. A theoretical study on the clusters Irn with n = 4, 6, 8, 10. *Chem. Phys. Lett.* **1997**, 276 (5–6), 334–338.

(29) Fielicke, A.; Kirilyuk, A.; Ratsch, C.; Behler, J.; Scheffler, M.; von Helden, G.; Meijer, G. Structure determination of isolated metal clusters via far-infrared spectroscopy. *Phys. Rev. Lett.* **2004**, *93*, 023401. (30) Oepts, D.; van der Meer, A. F. G.; van Amersfoort, P. W. The free-electron-laser user facility FELIX. *Infrared Phys. Technol.* **1995**, *36*, 297–308.

(31) Fielicke, A.; von Helden, G.; Meijer, G. Far-Infrared spectroscopy of isolated transition metal clusters. *Eur. Phys. J. D* 2005, 34, 83–88.

(32) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. Electronic-structure calculations on workstation computers. The

#### The Journal of Physical Chemistry C

program system TURBOMOLE. Chem. Phys. Lett. 1989, 162, 165-169.

(33) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(34) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, *105*, 9982–9985.

(35) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy adjusted abinitio pseudopotentials for the 2nd and 3rd row transition metals. *Theor. Chim. Acta* **1990**, *77*, 123–141.

(36) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design an assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(37) Harding, D. J.; Kerpal, C.; Meijer, G.; Fielicke, A. Unusual bonding in platinum carbido clusters. J. Phys. Chem. Lett. 2013, 4, 892–896.

(38) Ghiringhelli, L. M.; Gruene, P.; Lyon, J. T.; Rayner, D. M.; Meijer, G.; Fielicke, A.; Scheffler, M. Not so loosely bound rare gas atoms: finite-temperature vibrational fingerprints of neutral goldcluster complexes. *New J. Phys.* **2013**, *15*, 083003.

(39) Harding, D. J.; Kerpal, C.; Rayner, D. M.; Fielicke, A. Communication: The structures of small cationic gas-phase platinum clusters. *J. Chem. Phys.* **2012**, *136*, 211103.

(40) Ratsch, C.; Fielicke, A.; Kirilyuk, A.; Behler, J.; von Helden, G.; Meijer, G.; Scheffler, M. Structure determination of small vanadium clusters by density-functional theory in comparison with experimental far-infrared spectra. J. Chem. Phys. **2005**, 122, 15.

(41) Fielicke, A.; Ratsch, C.; von Helden, G.; Meijer, G. The farinfrared spectra of neutral and cationic niobium clusters:  $Nb_5^{0/+}$  to  $Nb_9^{0/+}$ . *J. Chem. Phys.* **2007**, *127*, 234306.

(42) Harding, D. J.; Gruene, P.; Haertelt, M.; Meijer, G.; Fielicke, A.; Hamilton, S. M.; Hopkins, W. S.; Mackenzie, S. R.; Neville, S. P.; Walsh, T. R. Probing the structures of gas-phase rhodium cluster cations by far-infrared spectroscopy. *J. Chem. Phys.* **2010**, *133*, 214304.

(43) Fielicke, A.; Gruene, P.; Haertelt, M.; Harding, D. J.; Meijer, G. Infrared Spectroscopy and Binding Geometries of Oxygen Atoms Bound to Cationic Tantalum Clusters. *J. Phys. Chem. A* **2010**, *114*, 9755–9761.

(44) Bowlan, J.; Harding, D. J.; Jalink, J.; Kirilyuk, A.; Meijer, G.; Fielicke, A. Communication: Structure of magnetic lanthanide clusters from far-IR spectroscopy:  $\text{Tb}_n^+$  (n = 5–9). *J. Chem. Phys.* **2013**, *138*, 031102.

(45) Bae, Y.-C.; Kumar, V.; Osanai, H.; Kawazoe, Y. Cubic magic clusters of rhodium stabilized with eight-center bonding: Magnetism and growth. *Phys. Rev. B* 2005, *72*, 125427.

Article