

Density functional theory calculations of vibrational spectra of rhodium oxide clusters

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Abstract

Predicted infrared vibrational spectra of low-energy isomers of rhodium cluster oxides, Rh_6O_m^+ ($m = 1-4$), are presented, based on structures calculated using density functional theory. The oxygen stretching frequencies are found to be characteristic of the oxygen binding mode. These simulated spectra provide a guide to future experimental measurements of the infrared multi-photon dissociation spectra, enabling assignment of the binding sites of oxygen atoms on the cluster. In favourable cases these calculations suggest that a determination of the underlying metal framework structure is possible.

1. Introduction

Transition metal (TM) clusters have been found to have highly size dependent properties[1], reflecting the important role played by structure in determining physical and chemical properties. Indeed, in some cases a single size of cluster is found to possess variable properties, such as multiple

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reaction rates[2, 3, 4, 5] or ionisation potentials[6, 7], which have been attributed to the presence of multiple geometric isomers of the cluster, each with its own behaviour. Computational investigations of the structures and properties[8, 9, 10] and the reactivity of clusters with small molecules support[11] this interpretation. Determination of the geometric structure of TM clusters is therefore a vital step towards understanding cluster properties.

A wide range of experimental methods have been applied in efforts to determine the structure of TM clusters. These include saturation adsorbate coverage[12, 13] and ion mobility measurements[14], which have been used to infer the co-existence of multiple isomers[15] of cobalt and gold clusters, respectively. These indirect methods are, however, only sensitive to isomers with significantly different reactivity or collision cross sections. There is relatively little direct information about the structure of gas-phase TM clusters. Trapped ion electron diffraction has been used to investigate the structure of silver cations, Ag_n^+ , $19 \leq n \leq 79$ [16], but is restricted in its applicability. Threshold photoionisation methods such as zero kinetic-energy photoelectron spectroscopy or mass analysed threshold ionisation spectroscopy, in conjunction with computational studies, have been used to determine the structures of several small clusters[17, 18]. These techniques, however, require the cluster to have relatively long-lived high principal quantum number Rydberg states, and extension to a wider range of clusters has proved to be challenging. Anion photoelectron spectroscopy has been used to investigate bare metal clusters[19] and metal oxide clusters[20, 21] with vibrational resolution.

A more recent approach to investigate the structure of TM clusters, which has already been applied to a wider range of clusters than the photoelectron

approaches, has been the use of photodissociation action spectroscopy. Here the dissociation of a species is measured as a function of the irradiation wavelength; with fragmentation serving as a signature that the original photon was absorbed. Tagging clusters with a rare gas atom can increase the sensitivity of the technique, as the weakly-bound rare gas atom is rapidly desorbed following the absorption of a few photons even in the far infrared (IR). Adsorption of a noble gas atom on the cluster surface is not believed to significantly affect the structure of the cluster itself[22, 23] although Gloess *et al.* report that the spectra of highly symmetric clusters may change in the presence of a physisorbed atom[23]. The use of rare gas tagging does, however, make the technique sensitive only to clusters that adsorb rare gas atoms. While this may make determination of the low-energy structures difficult, the approach can also be used in favourable cases to determine isomer-specific spectra[24].

Fielicke and co-workers have pioneered the use of infrared multi-photon dissociation (IRMPD) spectroscopy to investigate a range of charged and neutral TM clusters. The vibrational spectra of bare metal clusters[22, 24, 25, 26] have been probed by following the dissociation of noble gas tagged clusters, $M_n^{0/+}$ -Ar, while the adsorption of small molecules on clusters has been investigated by probing the vibrational modes of the adsorbed molecule[27, 28, 29, 30]. The binding sites of CO on rhodium clusters were reported to vary as a function of rhodium cluster size[27]. The structure of niobium oxide clusters, $Nb_nO_m^+$, $n < m$, was investigated[31] and IR absorption in two distinct regions was observed, attributed to atop- and bridge-bound oxygen atoms. Action spectroscopy techniques have also been used to measure the

UV/Vis spectra of metal clusters following the dissociation of argon tagged clusters[32, 23].

In order to determine the structure of a cluster, whether by diffraction, electronic or vibrational spectroscopy, comparison of the experimentally obtained spectra with simulated spectra is necessary in all but the smallest, simplest cases. This has largely been done once the experimental spectra have been recorded, in order to interpret the spectra in terms of the cluster structures likely to be present in the sample. In this article, by contrast, we present the IR spectra of Rh_6O_m^+ ($m = 1 - 4$) clusters in advance of any spectroscopic experiments being performed on these systems. We have previously reported the low-lying structural isomers of the naked Rh_6^+ clusters[11], which we calculated in order to account for the reactivity of Rh_6^+ with nitric oxide[5, 33]. The calculated spectra reported here will provide a direct means to compare with experiments planned for the free electron laser facility (FELIX) later this year.

2. Computational Methods

The methods used to predict likely low-energy structures have been described in detail previously[34] in relation to the study of cluster reactivity. Briefly, we have investigated a wide range possible structures for the oxides, Rh_6O_m^+ ($m = 1 - 4$), by the sequential addition of oxygen atoms in different binding modes and sites, starting from low-energy structures of Rh_6^+ [11]. Spin-unrestricted density functional theory (DFT) calculations were performed using the Gaussian03 package[35]. The PBE[36] exchange-correlation functional of Perdew, Burke and Ernzerhof was used

with the Stuttgart/Dresden (SDD) effective core potential (ECP) and basis functions[37] to describe rhodium and the aug-cc-pVDZ basis functions[38] used for oxygen. A range of spin multiplicities from doublet to dectet were considered for each isomer. Analytic second derivatives were used to calculate the IR spectra. The calculated stick spectra were gaussian broadened with a full width at half maximum height (fwhm) of 5 cm^{-1} to permit easier comparison with experimental spectra. Due to the multi-photon nature of IRMPD action spectroscopy, the calculated intensities are not expected to always match the experimental intensities[22].

3. Results

3.1. Monoxides

The simulated spectra of a range of low-energy Rh_6O^+ clusters with octahedral (O), trigonal prism (P) and capped square pyramid (C) metal cores, with the oxygen atom adsorbed in atop and bridge sites, are shown in Fig. 1. The clusters with an atop-bound oxygen atom show strongly absorbing modes in the range $880\text{-}920\text{ cm}^{-1}$ while those with the oxygen bridge-bound support modes from $580\text{ to }620\text{ cm}^{-1}$. The high frequency, strongly absorbing modes are found to be due, almost entirely, to motion of the oxygen atom. The binding mode of the oxygen atom was found to have more influence on the strongly absorbing lines in the spectra than the structure of the metal core. Based on the metal-oxygen vibrations alone, determination of the underlying metal structure may be difficult in some cases, particularly for O-bridge v. P-bridge and O-atop v. P-atop. However, in Fig. 1 we also show (magnified) detail of features located in the range corresponding with

metal-metal vibrations. In this region, the spectra for the cases mentioned above are distinct. Considered together, we predict there should be sufficient differences in each of the spectra to make structural assignment possible.

For some structures several spin multiplicities are very close in energy. We therefore also checked the influence of spin multiplicity on the appearance of our calculated spectra. We found that the low-frequency metal-metal modes could be influenced by spin multiplicity. On the other hand, the spectra for the metal-oxygen modes exhibited a much weaker dependence on spin state, provided that the change in spin state did not induce a significant change in the structure of the cluster[34]. Since it is only the low intensity (metal-metal) modes that appear to be affected, this does not appreciably change the overall appearance in the metal-oxygen region of most spectra with spin multiplicity.

3.2. Dioxides

The spectra of the four octet isomers of Rh_6O_2^+ lowest in energy are shown in Fig. 2. The three isomers lowest in energy are based on the octahedral metal framework while the fourth is based on the trigonal prism framework. All oxygen atoms were adsorbed bridge and/or hollow sites. The vibrational frequencies of the metal-oxygen modes in the dioxide clusters are similar to those of the monoxide clusters, with bridge-bound atoms having their most intense modes in the range 620 to 660 cm^{-1} , corresponding to blue-shifts of 20 to 40 cm^{-1} compared to monoxide clusters with the same metal core. The hollow site oxygens have modes in the range from 540 to 560 cm^{-1} . The vibrational modes are more complex than those of the monoxides, with coupling found between similarly-bound oxygen atoms in symmetric and

anti-symmetric stretches in the O-dibridge and O-dihollow clusters. For the O-dibridge cluster, both single and coupled oxygen modes (at *ca.* 470 and 530 cm^{-1}) were found. This led to more peaks in the spectrum than would be expected from our simple fingerprint interpretation. This finding does however underscore the important role that detailed computational studies can play in aiding the interpretation of experimental spectra. For the dioxide clusters each spectrum (based on metal-oxygen modes alone) is sufficiently distinct as to make unambiguous assignment of experimental structures a strong possibility. However, again we also show the enlarged detail of the region corresponding with the metal-metal modes in Fig. 2, emphasising the differences that are predicted to exist for clusters with the same metal framework but with a different arrangement of adsorbed oxygen atoms.

3.3. Trioxides

The predicted spectra of the low-energy structures identified for Rh_6O_3^+ clusters are shown in Fig. 3. The two lowest-energy isomers (Figs 3a and 3b) have distinctive spectra in the region corresponding with the metal-oxygen modes. The ^{16}O -trihollow has closely-grouped metal-oxygen modes, which might be expected from its relatively symmetric structure, while ^{12}C -tribridge has more widely-spread modes indicative of its low symmetry. The modes are also blue-shifted, by as much as 50 cm^{-1} , compared to the metal-oxygen modes of bridge-bound oxygen atoms on octahedral-based clusters. As with the dioxide clusters, many of the modes of the trioxide clusters couple two or more similarly-bound oxygen atoms, however, our analysis showed no coupling between bridge and hollow bound oxygens. The spectra of ^{16}O -dihollow-bridge (Fig. 3c) and ^{16}O -hollow-dibridge (Fig. 3d) have one mode

per oxygen atom at a frequency characteristic of the binding site of the atom, *i.e.* ^{4}O -dihollow-bridge has two modes in the hollow site region $540\text{-}580\text{ cm}^{-1}$ and one in the bridge region 640 cm^{-1} . These metal-oxygen frequencies may prove useful in identifying the binding sites of oxygen atoms on other sizes of cluster. In combination with the features present in the metal-metal region (Fig. 3), unambiguous assignment of the structures for these trioxide clusters appears likely.

3.4. *Tetroxides*

Two structures were predicted to dominate the population of Rh_6O_4^+ at low to medium energy[34]. The calculated spectra of these structures are shown in Fig. 4. The putative global minimum, based on an octahedral metal framework with a tetrahedral arrangement of oxygen atoms in hollow sites, has three modes at *ca.* $570\text{ to }585\text{ cm}^{-1}$ due to stretching modes coupling up to three of the oxygen atoms. Three additional features located at *ca.* $420\text{ to }435\text{ cm}^{-1}$ are due to oxygen wagging modes, which were not seen for the other clusters. A second higher-energy structure is based on a capped square pyramid with oxygen atoms in bridging and hollow sites. This structure supports one mode at *ca.* 580 cm^{-1} due to the hollow site oxygen and three modes from $660\text{ to }730\text{ cm}^{-1}$ due to modes coupling the three bridging oxygen atoms. Blue-shifts of *ca.* 20 cm^{-1} can be seen compared to the similar modes on the C-based trioxide (C-tribridge). Once again, these data indicate that it should be possible to make a reliable structural assignment from experiment. For completeness we again show these details in Fig. 4.

3.5. *Effect of Different Functionals*

As there is no clear preference for the choice of functionals to use for TM clusters, we have briefly investigated whether the choice of functional has an effect on the calculated vibrational spectra for these oxide clusters. We have recalculated the spectra of the dioxide geometries based on structures obtained from re-optimisation using the BLYP[39, 40] functional with the same basis functions and ECP as before. These spectra are compared in Fig. 5, showing that in the region corresponding with the metal-oxygen modes, both functionals support very similar features, although these peaks from the BLYP calculations are all red-shifted by 10–20 cm^{-1} compared with those calculated using PBE.

4. Conclusions

Our predicted vibrational spectra for a range of rhodium cluster oxides suggest that spectroscopic determination of the oxygen binding mode on rhodium clusters should be feasible in IRMPD experiments. In very favourable cases, such as the di- and tetroxides, it may also be possible to determine the underlying metal framework structure based on the metal-oxygen modes alone. The calculated intensities and frequencies of the metal-oxygen modes are much greater than those of the metal-metal modes, with no discernible differences in these features noted when using different exchange-correlation functionals. Each mode of oxygen binding can be associated with a fingerprint range of frequencies, with this range blue-shifted with increasing numbers of adsorbed oxygen atoms. Further, since we found no coupling between modes corresponding to oxygens in different bonding environments,

the number of vibrational modes in each fingerprint region equates in most cases with the number of oxygens adsorbed in that binding environment.

5. Acknowledgements

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References

- [1] J. L. Elkind, F. D. Weiss, J. M. Alford, R. T. Laaksonen, R. E. Smalley, J. Chem. Phys. 88 (1988) 5215.
- [2] Y. M. Hamrick, M. D. Morse, J. Phys. Chem. 93 (1989) 6494.
- [3] C. Adlhart, E. Uggerud, J. Chem. Phys. 123 (2005) 214709.
- [4] D. Harding, M. S. Ford, T. R. Walsh, S. R. Mackenzie, Phys. Chem. Chem. Phys. 9 (2007) 2130.
- [5] M. S. Ford, M. L. Anderson, M. P. Barrow, D. P. Woodruff, T. Drewello, P. J. Derrick, S. R. Mackenzie, Phys. Chem. Chem. Phys. 7 (2005) 975.
- [6] M. B. Knickelbein, S. Yang, J. Chem. Phys. 93 (1990) 1476.
- [7] M. B. Knickelbein, S. Yang, J. Chem. Phys. 93 (1990) 5760.
- [8] H. Grönbeck, A. Rosén, W. Andreoni, Phys. Rev. A 58 (1998) 4630.

- [9] Y.-C. Bae, H. Osanai, V. Kumar, Y. Kawazoe, Phys. Rev. B 70 (2004) 195413.
- [10] T. R. Walsh, J. Chem. Phys. 124 (2006) 204317.
- [11] D. Harding, S. R. Mackenzie, T. R. Walsh, J. Phys. Chem. B 110 (2006) 18272.
- [12] E. K. Parks, B. J. Winter, T. D. Klots, S. J. Riley, J. Chem. Phys. 94 (1991) 1882.
- [13] E. K. Parks, K. P. Kerns, S. J. Riley, Chem. Phys. 262 (2000) 151.
- [14] P. Weis, Int. J. Mass Spectrom. 245 (2005) 1.
- [15] P. Weis, T. Bierweiler, E. Vollmer, M. M. Kappes, J. Chem. Phys. 117 (2002) 9293.
- [16] M. N. Blom, D. Schooss, J. Stairs, M. M. Kappes, J. Chem. Phys. 124 (2006) 244308.
- [17] D.-S. Yang, P. A. Hackett, J. Elec. Spec. Rel. Phenom. 106 (2000) 153.
- [18] M. S. Ford, S. R. Mackenzie, J. Chem. Phys. 123 (2005) 084308.
- [19] H. Kietzmann, J. Morenzin, P. S. Bechthold, G. Ganteför, W. Eberhardt, D.-S. Yang, P. A. Hackett, R. Fournier, T. Pang, C. Chen, Phys. Rev. Lett. 77 (1996) 4528.
- [20] L.-S. Wang, H. Wu, S. R. Desai, Phys. Rev. Lett. 76 (1996) 4853.

- [21] S. M. E. Green, S. Alex, N. L. Fleischer, E. L. Millam, T. P. Marcy, D. G. Leopold, J. Chem. Phys. 114 (2001) 2653.
- [22] C. Ratsch, A. Fielicke, A. Kirilyuk, J. Behler, G. von Helden, G. Meijer, M. Scheffler, J. Chem. Phys. 122 (2005) 124302.
- [23] A. N. Gloess, H. Schneider, J. M. Weber, M. M. Kappes, J. Chem. Phys. 128 (2008) 114312.
- [24] A. Fielicke, C. Ratsch, G. von Helden, G. Meijer, J. Chem. Phys. 122 (2005) 091105.
- [25] A. Fielicke, C. Ratsch, G. von Helden, G. Meijer, J. Chem. Phys. 127 (2007) 234306.
- [26] P. Gruene, A. Fielicke, G. Meijer, J. Chem. Phys. 127 (2007) 234307.
- [27] A. Fielicke, G. von Helden, G. Meijer, D. B. Pedersen, B. Simard, D. M. Rayner, J. Phys. Chem. B 108 (2004) 14591.
- [28] A. Fielicke, G. v. Helden, G. Meijer, D. B. Pedersen, B. Simard, D. M. Rayner, J. Chem. Phys. 124 (2006) 194305.
- [29] I. Swart, A. Fielicke, B. Redlich, G. Meijer, B. M. Weckhuysen, F. M. F. de Groot, J. Am. Chem. Soc. 129 (2007) 2516.
- [30] I. Swart, F. M. F. de Groot, B. M. Weckhuysen, P. Gruene, G. Meijer, A. Fielicke, J. Phys. Chem. A 112 (2008) 1139.
- [31] A. Fielicke, G. Meijer, G. von Helden, J. Am. Chem. Soc. 125 (2003) 3659.

- [32] W. J. C. Menezes, M. B. Knickelbein, *J. Chem. Phys.* 98 (1993) 1856.
- [33] M. L. Anderson, M. S. Ford, P. J. Derrick, T. Drewello, D. P. Woodruff, S. R. Mackenzie, *J. Phys. Chem. A* 110 (2006) 10992.
- [34] D. J. Harding, R. D. L. Davies, S. R. Mackenzie, T. R. Walsh, *J. Chem. Phys.* 129 (2008) 124304.
- [35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.05*, Gaussian, Inc., Wallingford, CT, 2004.
- [36] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.

- [37] D. Andrae, U. Häußerman, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* 77 (1990) 123.
- [38] T. H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [39] A. D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [40] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 37 (1988) 785.

Figure Captions

Figure 1. Predicted IR spectra and relative energies of Rh_6O^+ clusters at the PBE/SDD+aug-cc-pVDZ level of theory. The structures and the displacement vector of the most intense mode are also shown; **a)** O-bridge (0.00 eV), **b)** O-atop (0.09 eV), **c)** P-atop (0.17 eV), **d)** P-bridge (0.18 eV), and **e)** C-bridge (0.25 eV). The metal-metal modes in the low-wavenumber region have been magnified for clarity.

Figure 2. Predicted IR spectra and relative energies of Rh_6O_2^+ clusters at the PBE/SDD+aug-cc-pVDZ level of theory; **a)** O-dibridge (0.0 eV), **b)** O-bridge-hollow (0.24 eV), **c)** O-dihollow (0.09 eV), and **d)** P-dibridge (0.30 eV). The metal-metal modes in the low-wavenumber region have been magnified for clarity.

Figure 3. Predicted IR spectra and relative energies of the lowest energy spin multiplicity of five low-energy isomers of Rh_6O_3^+ clusters, calculated at the PBE/SDD+aug-cc-pVDZ level of theory. From bottom to top; **a)** ^6O -trihollow (0.0 eV), **b)** ^4C -tribridge (0.28 eV), **c)** ^4O -dihollow-bridge (0.31 eV), **d)** ^6O -hollow-dibridge (0.32 eV), and **e)** ^6O -tribridge (0.33 eV). The

metal-metal modes in the low-wavenumber region have been magnified for clarity.

Figure 4. Predicted IR spectra and relative energies of Rh_6O_4^+ clusters at PBE/SDD+aug-cc-pVDZ level of theory; **a)** O-based (0.0 eV) and **b)** C-based (0.10 eV) structures. The metal-metal modes in the low-wavenumber region have been magnified for clarity.

Figure 5. Comparison of gaussian-broadened calculated IR spectra of Rh_6O_2^+ clusters using PBEPBE (black lines) and BLYP (red lines) functionals; **a)** O-dibridge, **b)** O-bridge-hollow, and **c)** O-dihollow.

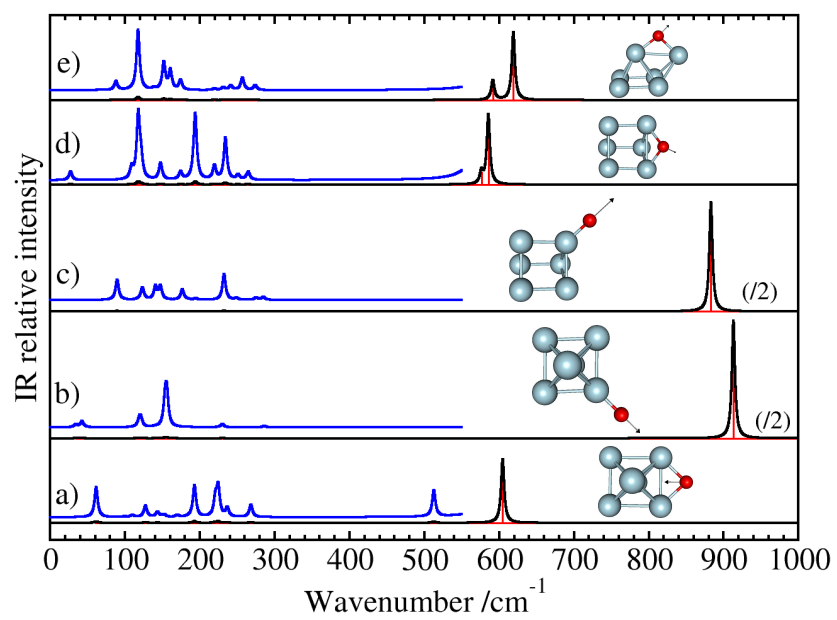


Figure 1:

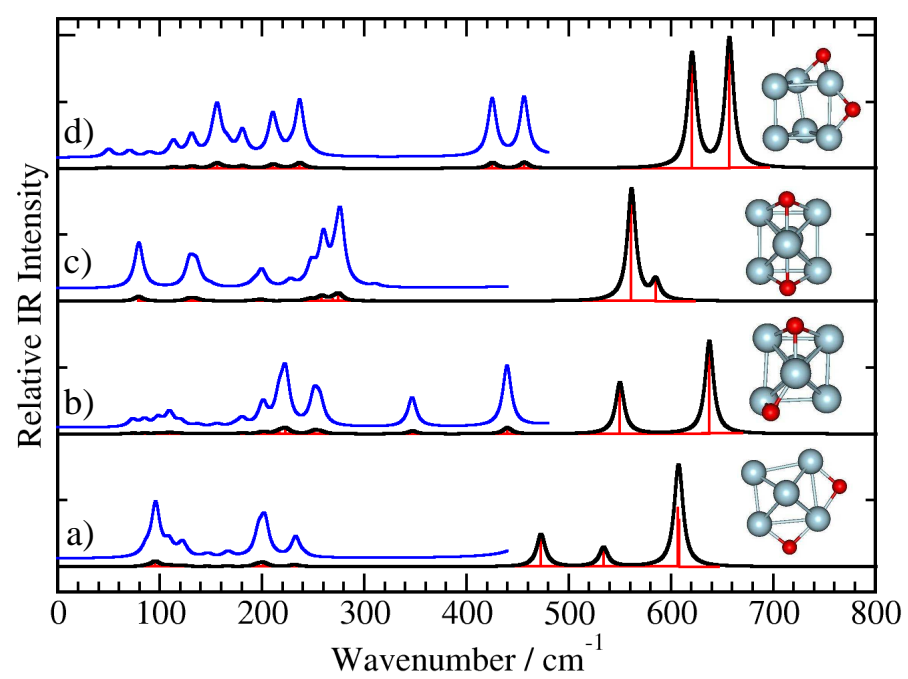


Figure 2:

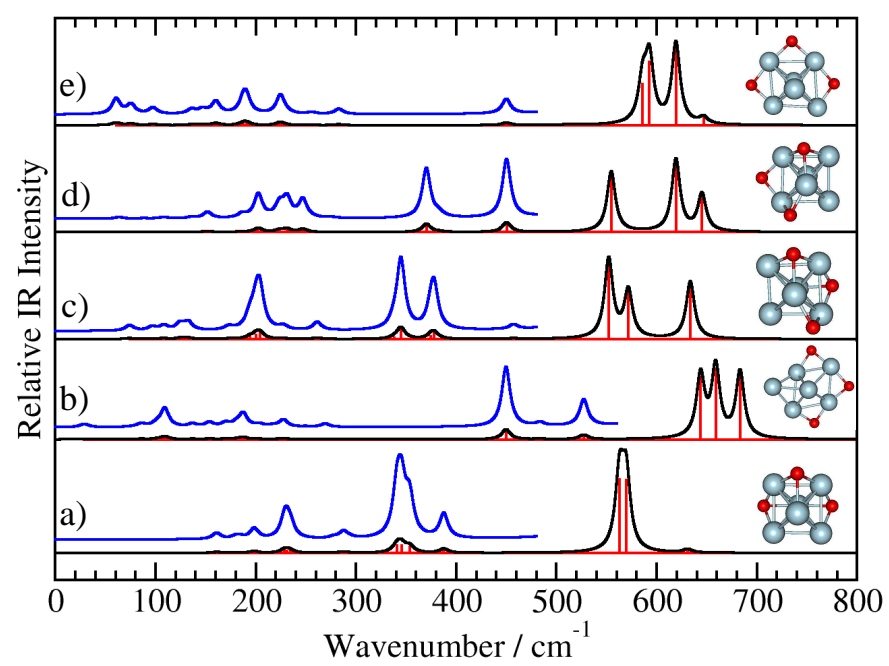


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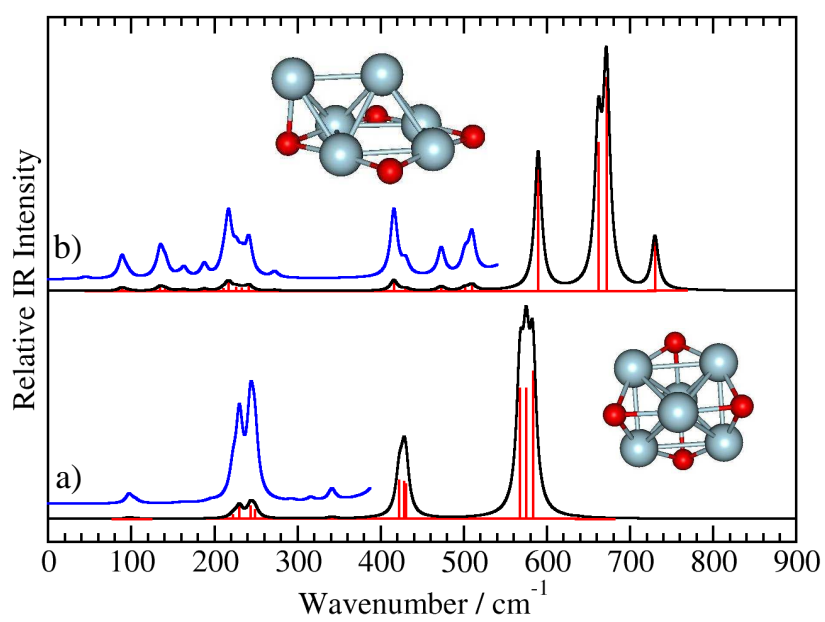


Figure 4:

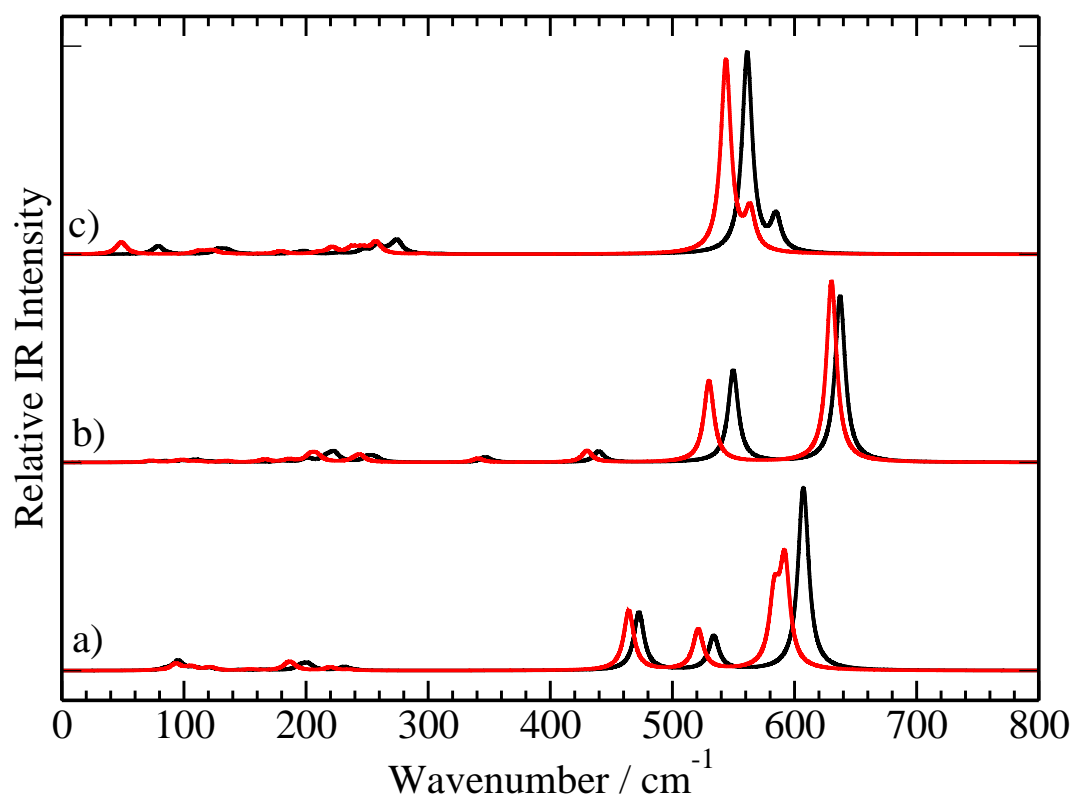


Figure 5: