

Highly Unsaturated Platinum and Palladium Carbenes PtC₃ and PdC₃ Isolated and Characterized in the Gas Phase

Dror M. Bittner, Daniel P. Zaleski, David P. Tew, Nicholas R. Walker,* and Anthony C. Legon*

Abstract: Carbenes of platinum and palladium, PtC₃ and PdC₃, were generated in the gas phase through laser vaporization of a metal target in the presence of a low concentration of a hydrocarbon precursor undergoing supersonic expansion. Rotational spectroscopy and *ab initio* calculations confirm that both molecules are linear. The geometry of PtC₃ was accurately determined by fitting to the experimental moments of inertia of twenty-six isotopologues. The results are consistent with the proposal of an autogenic isolobal relationship between O, Au⁺, and Pt atoms.

The importance of industrial catalysis by platinum and palladium has prompted extensive studies of their gas-phase chemistry.^[1] Each metal atom is known to initiate cleavage of the C–H and C=C bonds of hydrocarbon precursors. We believe that the present study provides the first pure rotational spectra of platinum and palladium carbenes isolated in the gaseous phase. PtC₃ and PdC₃ (each in a ¹Σ state) were generated through laser vaporization of solid Pt/Pd in the presence of a gas sample undergoing supersonic expansion and containing a low concentration (typically 1%) of a hydrocarbon precursor in a buffer gas of argon. Analysis of the rotational spectra reveals that each molecule has a linear geometry and an MCCC connectivity (where M is the metal atom). The results are a successful test of a model proposed by Pyykkö et al.^[2] which suggests that platinum can be regarded as the isoelectronic and isolobal counterpart of a chalcogen for the purposes of predicting structure and reactivity trends.

A wide range of hydrocarbon precursors, each tested individually, were found to allow the generation of PtC₃ and

PdC₃. For PdC₃, the range of effective precursors includes C₃H₄ (allene), C₂H₂, C₂H₄, CH₄, and C₄H₄O (furan). For PtC₃, the range is narrower, including C₃H₄ (allene), C₂H₄, and CH₄, all of which were found to be effective. Broadband microwave spectra of the target molecules were recorded between 6.5 and 18.5 GHz (Figure 1) using a spectrometer described

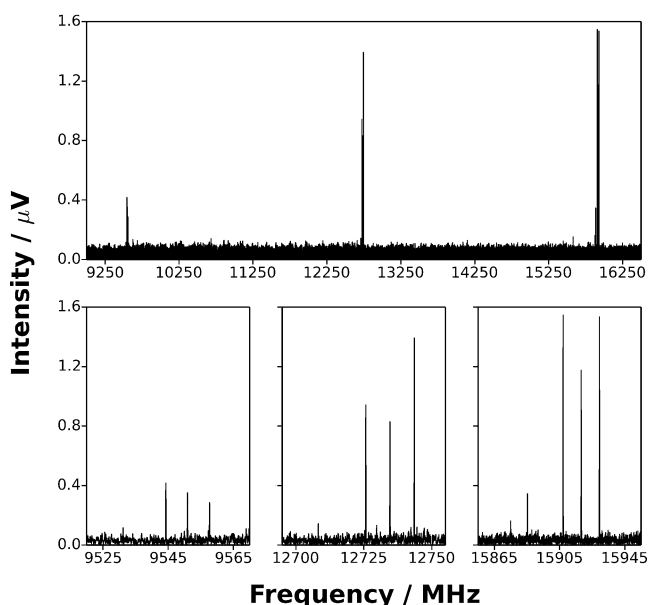


Figure 1. Top: The broadband rotational spectrum (showing the 9 GHz to 16.5 GHz region) averaged over 480 000 free induction decays (FIDs) and recorded while vaporizing a Pt source in the presence of CH₄ under the conditions described in the text. Bottom: $J'' \rightarrow J' = 6 \rightarrow 5$ transitions of each of ¹⁹⁴PtC₃, ¹⁹⁵PtC₃, ¹⁹⁶PtC₃, and ¹⁹⁸PtC₃ are displayed in the bottom-left panel. $J'' \rightarrow J' = 7 \rightarrow 6$ and $J'' \rightarrow J' = 8 \rightarrow 7$ transitions of the isotopologues listed above are shown in the bottom-center and bottom-right panels, respectively.

previously in detail.^[3] Each spectrum was assigned and fitted to the Hamiltonian of a linear molecule using Western's program PGOPHER.^[4] The low number of $J'' \rightarrow J'$ transitions within the bandwidth of the spectrometer required that centrifugal distortion constants be fixed at results calculated *ab initio* by an approach described previously.^[5] Structure optimizations, reaction energies, and orbital energy level diagrams were calculated using the MOLPRO package^[6] at the CCSD(T) level of theory.^[7] The basis set combination employed the aug-cc-pwCV5Z basis set for each C atom and the aug-cc-pwCV5Z-PP basis set for each of Pt and Pd.^[8] The ECP-28-MDF and ECP-60-MDF effective core potentials were used to account for scalar relativistic effects on Pd and

[*] D. M. Bittner, Dr. D. P. Zaleski, Dr. N. R. Walker
School of Chemistry, Bedson Building, Newcastle University
Newcastle upon Tyne, Tyne and Wear, NE1 7RU (UK)
E-mail: nick.walker@newcastle.ac.uk

Dr. D. P. Tew, Prof. Dr. A. C. Legon
School of Chemistry, University of Bristol
Bristol, BS8 1TS (UK)
E-mail: a.c.legon@bristol.ac.uk

Dr. D. P. Zaleski
Current address: Argonne National Laboratory
Chemical Sciences and Engineering
9700 S. Cass Ave., Bldg. 200, Lemont, IL 60439 (USA)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201511646>.

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Pt, respectively,^[8] with all electrons included in the correlation treatment. Electric dipole moments and centrifugal distortion constants were calculated with the GAUSSIAN09 package^[9] at the MP2 level of theory using a basis set combination consisting of aug-cc-pVTZ on C atoms and aug-cc-pVTZ-PP on Pd and Pt atoms.^[8] Selected results of spectroscopic fits are shown in Table 1 with complete details for all isotopologues provided in the Supporting Information. The standard deviations of all fits are consistent with the measured linewidth (FWHM) of 120 kHz. Neither PtC₂ nor PdC₂ were identified despite a careful search of the spectra. Rotational transitions of both PtC^[10] (measured previously) and PdC lie higher in frequency than the upper limit of the spectrometer. Where PdC₃ was generated from a furan precursor, intense transitions of PdCO^[11] were detected in addition to those assigned to PdC₃.

Table 1: Spectroscopic parameters of PtC₃ and PdC₃.^[a]

Species	B_0 [MHz]	$[D_j \times 10^2]^{[b]}$ [kHz]	$\chi_{aa}^{(105\text{Pd})}$ [MHz]	σ [kHz]	N
¹⁹⁴ Pt ¹² C ¹² C ¹² C	1592.94589(35)	[6.2]	–	5.0	3
¹⁹⁴ Pt ¹³ C ¹³ C ¹³ C	1486.74426(60)	[5.4]	–	11.1	4
¹⁹⁴ Pt ¹² C ¹² C ¹³ C	1522.47541(52)	[5.6]	–	9.1	3
¹⁹⁴ Pt ¹² C ¹³ C ¹² C	1560.77071(27)	[6.0]	–	3.4	2
¹⁹⁴ Pt ¹³ C ¹² C ¹² C	1585.00114(43)	[6.2]	–	6.1	3
¹⁰⁶ Pd ¹² C ¹² C ¹² C	1702.33446(43)	[9.5]	–	6.3	4
¹⁰⁵ Pd ¹² C ¹² C ¹² C	1705.89034(57)	[9.6]	35.88(43)	14.5	9
¹⁰⁶ Pd ¹³ C ¹³ C ¹³ C	1599.5465 ^[c]	[8.4]	–	–	1

[a] Results of selected spectroscopic fits illustrating the dependence of rotational (B_0) and centrifugal distortion (D_j) constants on isotopic substitution. $\chi_{aa}^{(105\text{Pd})}$ denotes the nuclear quadrupole coupling constant of the ¹⁰⁵Pd atom. N and σ are the number of fitted transitions and the standard deviation of the fit, respectively. Further results are presented in Table S1 in the Supporting Information. [b] Centrifugal distortion constants are fixed to results calculated ab initio at the MP2/AVTZ level. [c] Result calculated from a single transition frequency.

Spectra were measured for isotopologues of PtC₃ and PdC₃ that contain the ¹³C isotope to ensure assignment of the correct molecular carriers and allow precise determination of the molecular geometries. Experimental data are available only for the ground vibrational state of each molecule allowing an effective r_0 geometry to be fitted in each case. The experimental results are consistent with two possibilities for each molecule: 1) a geometry that is slightly bent at equilibrium but quasilinear in the $\nu=0$ state, and 2) an equilibrium (r_e) geometry that is linear. The ab initio calculations suggest that both molecules are linear at equilibrium. The intensities of PdC₃ transitions were found to be highly dependent on the choice of precursor, in the order C₃H₄ > C₂H₄ > CH₄. Transition intensities were lower when the population of PdC₃ was divided across many isotopic permutations and isotopically enriched allene is prohibitively expensive. These factors prevented measurement of the spectrum of any PdC₃ isotopologue that contains both ¹²C and ¹³C isotopes. The intensities of PtC₃ transitions were insensitive to the choice of precursor and it was possible to

generate and record spectra for many isotopic permutations of PtC₃ (from the set of ¹⁹⁴Pt, ¹⁹⁵Pt, ¹⁹⁶Pt, ¹⁹⁸Pt, ¹²C, and ¹³C atoms) using samples prepared by mixing ¹²CH₄ and commercially supplied ¹³CH₄. It was also found that PtC₃ can be generated from a mixture of ¹²C₂H₂ and ¹³CH₄ precursors with the result that the spectra of ¹⁹⁴Pt¹²C¹²C¹³C, ¹⁹⁴Pt¹²C¹³C¹²C, and ¹⁹⁴Pt¹³C¹²C¹²C were detected with equal intensities. The observation that the ¹³C isotope does not preferentially occupy an end position of the C₃ subunit strongly implies that the C≡C bond of C₂H₂ cleaves during the sequence of reactions that generates PtC₃ from this set of precursors.

The present study is believed to be the first to characterize MC₃ units by rotational spectroscopy. Transition-metal dicarbides, such as ScC₂ and YC₂, have been studied previously.^[12] The dipole moments of PdC₃ and PtC₃ are calculated at the MP2 level to be 6.1 and 5.6 D, respectively. The lengths of bonds within PtC₃ were fitted to experimentally determined rotational constants using Kisiel's STRFIT.^[13] Spectra were measured for 26 distinct isotopologues of PtC₃ where the set includes every permutation of C₃ that it is possible to generate from ¹²C and ¹³C isotopes. The bond lengths thus determined are compared with those in isolated PtC, C₃ and OC₃ molecules in Table 2. The r_0 geometry of PtC₃ is in good agreement with the r_e geometry calculated at the CCSD(T) level. The Pt–C bond in PtC₃ is longer than found in diatomic PtC^[10] by 0.053 Å. There are similarities between $r(\text{MC})$ in PtC₃ and in PtCO,^[14] and also in changes when these molecules form from their component Pt and C₃/CO subunits. The $r(\text{MC})$ parameter in PtC₃ is shorter than the same quantity in PtCO by 0.031 Å. The first C=C bond (that which is contiguous with the Pt–C bond) of PtC₃ is longer than the C=C bond in isolated C₃ by 0.022 Å. The set of isotopologues studied is less extensive for PdC₃ than for PtC₃ and does not permit determination of all bond lengths from the experimental data. If the lengths of C=C bonds within the molecule are fixed as shown in Table 2, $r(\text{PdC})$ is determined to be

Table 2: Structural parameters of PtC₃, PdC₃, and related molecules.^[a]

Species ^[a]	$r(\text{MC})$ [Å]	$r(\text{CC1})$ [Å]	$r(\text{CC2})$ [Å]
PtC ^[b]	1.679	–	–
C ₃ (r_0) ^[b]	–	1.277247(2)	1.277247(2)
OC ₃ (r_0) ^[b]	1.150	1.306	1.254
PtC ₃ (r_0)	1.7315(14)	1.2993(19)	1.2759(11)
PtC ₃ (r_e)	1.7280	1.2942	1.2836
PdC ₃ (r_0)	1.79898(4)	[1.3009] ^[c]	[1.2789] ^[c]
PdC ₃ (r_e)	1.7962	1.2958	1.2866
	$r(\text{MC})$ [Å]	$r(\text{CO})$ [Å]	
CO	–	1.128	
PtCO (r_0) ^[d]	1.7625(4)	1.1466(6)	
PdCO (r_0) ^[d]	1.8447(1)	1.1374(2)	

[a] $r(\text{MC})$ denotes the bond between the metal atom (or oxygen atom in OC₃) and its coordinated carbon. $r(\text{CC1})$ denotes the C=C bond nearest to the metal atom with $r(\text{CC2})$ used to label the other. r_0 values are determined experimentally and r_e values are calculated ab initio. [b] Data from Refs. [10, 19, 22]. [c] Each number in square brackets is fixed to the result obtained by correcting the r_e value calculated ab initio for PdC₃ for the difference between the r_0 and r_e values determined for the equivalent parameter in PtC₃. [d] Data from Refs. [11, 14].

1.79898(4) Å. Values of vibrational wavenumbers calculated ab initio are provided in the Supporting Information.

The described results confirm that the heavier elements of Group 10 can form linear arrangements similar to that previously identified for Ni₂C₃.^[15] The detected palladium/platinum carbenes are amongst the smallest to be structurally characterized.^[16] There is a correspondence between the linear geometries of the MC₃ units identified herein and the linear carbon chains that are interceded by Pt/Pd atoms which are a feature of many synthetic coordination polymers.^[17] The results are also interesting in the context of the wider chemistry of metal atoms in hydrocarbon plasmas. Early transition metals are known to react with hydrocarbon precursors to generate metallocarbohydrides (met-cars).^[18] Late transition metals show no general tendency to form such extended structures. The present experiment does not unambiguously distinguish the reaction sequences (or networks of competing reactions) that generate PdC₃ and PtC₃. It is possible that a fraction of the population of each forms through gas-phase association of individual metal atoms with intact C₃ or other units generated independently of any metal atom.^[19] The energy changes accompanying the M + C₃ → MC₃ association reactions to yield linear MC₃ units are calculated to be −295 kJ mol^{−1} and −417 kJ mol^{−1} when M = Pd and M = Pt, respectively (detailed calculations are shown in the Supporting Information). However, it is also possible that the metals themselves initiate the sequence of chemical reactions that leads to dehydrogenation of the precursor. There is extensive evidence from previous studies that both Pt and Pd atoms undergo bond-insertion and cleavage reactions with hydrocarbons.^[1a,20] MCH₂ and MCCH₂ have both been generated^[1a,b,21] previously by a laser vaporization/supersonic expansion method, characterized by matrix isolation spectroscopy, and are also likely to be generated under the present experimental conditions. Transition frequencies of MCH₂ are expected to be above the upper frequency limit of the spectrometer and both MCH₂ and MCCH₂ will have comparatively low dipole moments which significantly decrease the intensity of their rotational transitions relative to those of MC₃.

An empirical model proposed by Pyykkö et al.^[2a] provides a chemical rationalization for an enhanced stability of MC₃ relative to MC₂ or MC₄. Calculations of the geometries of CAu²⁺, CAu³⁺, Pt₂C, Pt₂C₃, and Au₂C₂ revealed analogies between the behavior of each of Au⁺ and Pt and a chalcogen atom such as O.^[2a] Within this model, the σ hole on platinum arising from the 5d¹⁰6s⁰ configuration is analogous to the 2pσ⁰ hole on oxygen, and the 5dπ orbitals of platinum participate in π-bonding interactions analogous to those involving the 2pπ orbital of oxygen. The existence of a family of stable molecules was thus predicted. An orbital energy level diagram for PtC₃ is presented in Figure S1 in the Supporting Information. There are striking similarities between the geometries of MC₃ measured during the present work and that reported earlier for OC₃ by Brown et al.^[22] Applying the model of Pyykkö et al., PtCO, PtC, and Pt₂C₃ are analogues of the well-known, stable oxocarbons carbon dioxide, monoxide, and suboxide, respectively, each of which have been known since the 19th century. Similarly, PtSi^[23] can

be regarded as an analogue of SiO. The oxocarbon analogue of Pt₂C₂ would be ethylene dione,^[24] a transient species characterized, only through spectroscopy, for the first time in 2015. This model can thus explain why PtCO, PtC, and PtC₃, but not yet PtC₂, have been detected. The results of the present work thus support the suggestion that platinum can be regarded an isoelectronic, isolobal counterpart of oxygen. The proposal can be further assessed with reference to previous works.

Reports of clusters containing multiple carbon and platinum or palladium atoms are scarce. The adsorption of, and reactions of, CH₄ and CO on Pt_n clusters^[1e] and the structures of Pt_nO_m clusters^[4d] have been studied. Harding et al. identified a Pt₃C⁺ cluster ion^[25] for which the geometry is analogous to a carbonate ion and hence consistent with the prediction of the model provided by Pyykkö et al.^[2] The geometries of other platinum/carbon clusters, which have not yet been observed or characterized, may perhaps be predicted by analogy with other oxocarbons. For example, mellitic anhydride (C₁₂O₉) is known to be stable, suggesting that Pt₉C₁₂ might be generated in an equivalent structural form. An experimental study^[26] of AuC_n⁺ and CuC_n⁺ revealed ion intensities in the mass spectra that are significantly stronger where *n* = 3 than for clusters of other sizes.^[26] Some caution must be exercised in drawing conclusions about the thermodynamic stability of AuC₃⁺ relative to other cluster sizes from these results. As in the present work, the experiment performed by Ticknor et al.^[26] did not unambiguously distinguish between various factors that contribute to observed spectral intensities. It is likely that C₃ was generated with a significantly higher abundance^[19] than C₂ within the expanding gas sample and this may cause the generation of AuC₃⁺ to be favored over the generation of clusters of other sizes, regardless of the thermodynamic stability of AuC₃⁺. Indeed, during a previous study, signals for NiC₃⁺ and NiC₆⁺ were detected in mass spectra with higher intensity than units containing 1, 2, 4, or 5 carbon atoms,^[27] although the Ni⁺ ion is not isoelectronic and isolobal with O. However, the reported fragmentation behavior of AuC_n⁺ is also notable. Clusters where *n* is odd lose only the metal atom on photodissociation whereas those with an even value of *n* display an additional loss channel corresponding to the loss of an odd number of carbon atoms. The overall result is that chains (either isolated or attached to the metal ion) containing an odd number of carbon atoms tend to be formed during photofragmentation, consistent with the proposal of Pyykkö et al. The perspective thus emerging from the collected results of spectroscopic experiments is that the proposal^[2a] of an autogenic isolobal relationship of Pt and Au⁺ centers with the O atom is powerful and useful with respect to structural trends in gas-phase clusters that contain Pt, Pd, Au⁺, and C centers.

Acknowledgements

The authors thank the European Research Council (CPFTMW-307000) for project funding, the Engineering and Physical Sciences Research Council (U.K.) for the award of a DTA studentship (EPK5028931) to D.M.B., and

the EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London. A.C.L. thanks the University of Bristol for a Senior Research Fellowship. D.P.Z. thanks Newcastle University for the award of a Faculty of SAgE Research Fellowship. D.P.T. thanks the Royal Society for a University Research Fellowship.

Keywords: ab initio calculations · carbenes · palladium · platinum · rotational spectroscopy

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 3768–3771
Angew. Chem. **2016**, *128*, 3832–3835

- [1] a) H.-G. Cho, L. Andrews, *J. Phys. Chem. A* **2004**, *108*, 6272–6278; b) J. J. Carroll, J. C. Weisshaar, P. E. M. Siegbahn, C. A. M. Wittborn, M. R. A. Blomberg, *J. Phys. Chem.* **1995**, *99*, 14388–14396; c) X.-G. Zhang, R. Liyanage, P. B. Armentrout, *J. Am. Chem. Soc.* **2001**, *123*, 5563–5575; d) D. J. Harding, A. Fielicke, *Chem. Eur. J.* **2014**, *20*, 3258–3267; e) D. J. Harding, C. Kerpál, G. Meijer, A. Fielicke, *Angew. Chem. Int. Ed.* **2012**, *51*, 817–819; *Angew. Chem.* **2012**, *124*, 842–845.
- [2] a) P. Pyykkö, M. Patzschke, J. Suurpere, *Chem. Phys. Lett.* **2003**, *381*, 45–52; b) L. G. M. de Macedo, P. Pyykkö, *Chem. Phys. Lett.* **2008**, *462*, 138–143.
- [3] D. P. Zaleski, S. L. Stephens, N. R. Walker, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25221–25228.
- [4] PGOPHER, a Program for Simulating Rotational, Vibrational, and Electronic Structure, C. M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>.
- [5] D. P. Zaleski, S. L. Stephens, D. P. Tew, D. M. Bittner, N. R. Walker, A. C. Legon, *Phys. Chem. Chem. Phys.* **2015**, *17*, 19230–19237.
- [6] Molpro: a general-purpose quantum chemistry program package: H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, *WIREs Comput. Mol. Sci.* **2012**, *2*, 242–253.
- [7] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.
- [8] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurmooorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.
- [9] Gaussian 09, Revision D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford, CT, USA, **2009**.
- [10] a) T. C. Steimle, K. Y. Jung, B. Z. Li, *J. Chem. Phys.* **1995**, *102*, 5937–5941; b) C. Qin, R. Zhang, F. Wang, T. C. Steimle, *Chem. Phys. Lett.* **2012**, *535*, 40–43.
- [11] N. R. Walker, J. K. H. Hui, M. C. L. Gerry, *J. Phys. Chem. A* **2002**, *106*, 5803–5808.
- [12] a) J. Min, D. T. Halfen, L. M. Ziurys, *Chem. Phys. Lett.* **2014**, *609*, 70–75; b) D. T. Halfen, J. Min, L. M. Ziurys, *Chem. Phys. Lett.* **2013**, *555*, 31–37.
- [13] Z. Kisiel, *J. Mol. Spectrosc.* **2003**, *218*, 58–67.
- [14] C. J. Evans, M. C. L. Gerry, *J. Phys. Chem. A* **2001**, *105*, 9659–9663.
- [15] R. E. Kinzer, C. M. L. Rittby, W. R. M. Graham, *J. Chem. Phys.* **2008**, *128*, 064312.
- [16] C. C. Womack, K. N. Crabtree, L. McCaslin, O. Martinez, R. W. Field, J. F. Stanton, M. C. McCarthy, *Angew. Chem. Int. Ed.* **2014**, *53*, 4089–4092; *Angew. Chem.* **2014**, *126*, 4173–4176.
- [17] a) H. F. Wittmann, R. H. Friend, M. S. Khan, J. Lewis, *J. Chem. Phys.* **1994**, *101*, 2693–2698; b) C. R. Horn, J. A. Gladysz, *Eur. J. Inorg. Chem.* **2003**, 2211–2218.
- [18] a) L.-S. Wang, X. Li, *J. Chem. Phys.* **2000**, *112*, 3602–3608; b) R. E. Kinzer, C. M. L. Rittby, W. R. M. Graham, *J. Chem. Phys.* **2006**, *125*, 074513.
- [19] A. Van Orden, R. J. Saykally, *Chem. Rev.* **1998**, *98*, 2313–2358.
- [20] H.-G. Cho, L. Andrews, *Organometallics* **2009**, *28*, 1358–1368.
- [21] V. J. F. Lapoutre, B. Redlich, A. F. G. van der Meer, J. Oomens, J. M. Bakker, A. Sweeney, A. Mookherjee, P. B. Armentrout, *J. Phys. Chem. A* **2013**, *117*, 4115–4126.
- [22] R. D. Brown, P. D. Godfrey, P. S. Elmes, M. Rodler, L. M. Tack, *J. Am. Chem. Soc.* **1985**, *107*, 4112–4115.
- [23] S. A. Cooke, M. C. L. Gerry, D. J. Brugh, R. D. Suenram, *J. Mol. Spectrosc.* **2004**, *223*, 185–194.
- [24] A. R. Dixon, T. Xue, A. Sanov, *Angew. Chem. Int. Ed.* **2015**, *54*, 8764–8767; *Angew. Chem.* **2015**, *127*, 8888–8891.
- [25] D. J. Harding, C. Kerpál, G. Meijer, A. Fielicke, *J. Phys. Chem. Lett.* **2013**, *4*, 892–896.
- [26] B. W. Ticknor, B. Bandyopadhyay, M. A. Duncan, *J. Phys. Chem. A* **2008**, *112*, 12355–12366.
- [27] J. E. Reddic, M. A. Duncan, *Chem. Phys. Lett.* **1997**, *264*, 157–162.

Received: December 15, 2015

Published online: February 15, 2016