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Methane Activation

Activated Methane on Small Cationic Platinum Clusters**

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The catalytic activation of C–H bonds in small hydrocarbons, particularly methane, is a reaction that is of significant technological interest, as it allows valuable, functionalized products to be made from plentiful, cheap feedstocks. However, even on well-characterized platinum surfaces, the determination of the details of methane activation, in particular the earliest steps, remains difficult.[1,2] Challenges include the weak physisorption of molecular methane on platinum surfaces, its ready dissociation, and the difficulty associated with determining hydrogen atom positions in many surface experiments, as hydrogen atoms are weak scatterers of X-rays or electrons and have no electronic core levels.[3] Despite these challenges, Yoshinobu et al. have used infrared reflection absorption spectroscopy to show that CH_4 adsorbed on Pt(111) has at most C_{3v} symmetry.[4] Öström et al. have determined the adsorption geometry of methane on Pt(977) using X-ray absorption spectroscopy,[5] reporting methane to bind by a single hydrogen atom, though they were unable to determine whether it was bound atop or in hollow sites. Partially dehydrogenated reaction intermediates/products, including methyl, methylene, and methylidyne, have been extensively studied (see for example Ref. [6]).

The reactions of methane with platinum atoms and clusters have been studied in some detail.[7] In the case of small ionic clusters reacting with CH_4 under single collision conditions, $Pt_n[C,2H]^+$ complexes were found to be the favored products.[8–10] There have been a number of computational studies of the interactions of platinum clusters[11–13] and surfaces[5,14,15] with methane, primarily using density functional theory (DFT). Such calculations are challenging, owing to the large system size, number of electrons and possible paths, and the fact that several electronic states and crossings between them may need to be treated.[13] Experimental spectroscopic characterization of these species, particularly the reaction intermediates, can therefore provide important information about their structures and benchmark data for theory.

Recently, we have demonstrated the possibility of forming reactive intermediate species under thermalized conditions in a flow reactor.[16] This approach was unsuccessful for the Pt_n^+–CH_4 system owing to rapid dehydrogenation of CH_4, apparently occurring in the metal plasma generated during the laser ablation process. Herein, we use a different method to stabilize complexes along the entrance channel of the gas-phase reactions, specifically $Pt_{3-5}CH_4^+$, which allows their spectroscopic characterization. This is achieved by ligand exchange between CH_4 and Ar on cold pre-formed $Pt_nAr_m^+$ complexes [Eq. (1)]:

$$Pt_nAr_m^+ + CH_4 \rightarrow Pt_nAr_{m-p}CH_4^+ + p\,Ar \qquad (1)$$

The modified experimental setup is shown in Figure 1. Platinum clusters are formed by laser ablation from an isotopically enriched ^{194}Pt target. Adding 0.2% Ar to the He carrier gas and cooling the thermalization channel to 180 K yields a distribution (without CH_4) of clusters $Pt_nAr_{0-5}^+$ (for experimental details, see Ref. [17]). After expansion from the source, the cluster beam is crossed by a molecular beam of CH_4 from a pulsed valve. The reaction products are analyzed in a time-of-flight mass spectrometer. Under these (near)-single-collision conditions, formation of $Pt_nCH_4Ar_{0-4}^+$ complexes is observed. The adsorption energy must be efficiently removed by the evaporating Ar atoms, quenching the complex into an early local minimum on the dehydrogenation reaction pathway. Pt_n^+ clusters without Ar ligands form primarily $Pt_nCH_2^+$ complexes, in agreement with earlier experiments under single-collision conditions.[8–10] Similar changes in reactivity with argon coverage, from rapid dehydrogenation to sticking of CH_4, have been observed for Pt^+ atomic ions.[18] The Ar coverage dependence of the reactions of $Rh_nAr_m^+$ with methane has been investigated in detail,[19] showing the formation of $Rh_n[C,4H]^+$ and $Rh_n[C,2H]^+$ complexes, while most bare Rh_n^+ clusters (except Rh_2^+) are essentially unreactive towards methane. Mass spectrometry alone cannot, however, provide detailed information about the structures of the complexes.

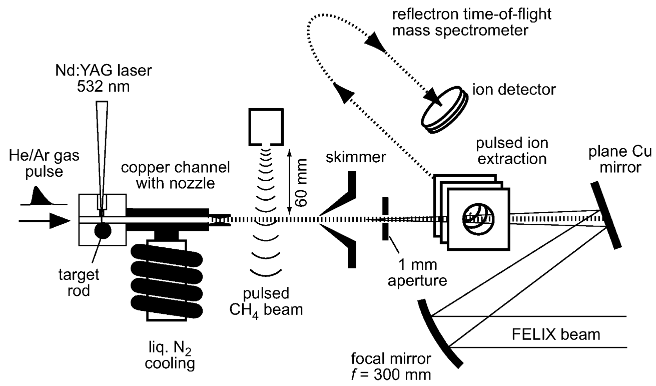

Figure 1. The crossed-beam experimental setup.

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In the present study, experimental vibrational spectra of $Pt_nCH_4Ar_{1-4}^+$ complexes are obtained between 650 and 1600 cm^{-1} by infrared multiple photon dissociation (IR-MPD), using the free electron laser for infrared experiments (FELIX).[20] This range covers the characteristic C–H deformation modes of CH_2, CH_3, and CH_4 species. To aid in the structural identification we have also performed DFT calculations on a range of $Pt_n[C,4H]^+$ species at the TPSS/def2-TZVP level of theory[21] using TURBOMOLE.[22] The initial structures for the platinum clusters were low-energy geometries and spin multiplicities that we have identified from a combined IR-MPD and computational study of the small bare Pt clusters.[23] IR-MPD spectra and the best-matching calculated spectra are shown in Figure 2. The modes are assigned based on the motion of the non-bonding hydrogen atoms. A range of alternative structures including partially dehydrogenated, η_1-CH_4 and η_3-CH_4 complexes were also considered, but provide less good matches to the experimental spectra, examples are shown in the Supplementary Information.

The experimental spectra of the [C,4H] complexes have features in the range 1140–1560 cm^{-1}, consistent with symmetry-induced splitting of the e (1534 cm^{-1}) and t_2 (1306 cm^{-1}) vibrational modes of free methane. The broad splitting, particularly for $n = 4,5$, suggests a significant degree of activation of the C–H bonds in the complexes. For $n = 3$, the calculated spectrum that best matches the experimental spectrum is not that of the lowest-energy isomer we have found, a partially dehydrogenated species, but of molecularly adsorbed η_2-CH_4, bound by two H atoms to one Pt atom in the cluster. For $n = 4$, the molecularly bound species is the lowest-energy structure we have found, while for $n = 5$, molecularly and dissociatively adsorbed species are essentially isoenergetic. In both cases, η_2-CH_4 molecularly adsorbed species provide the best matches to the experimental spectra. In the trigonal bipyramid Pt_5^+ there are two distinct types of Pt atom, that is, three- and four-coordinate, to which the CH_4 can bind. The calculated total energies in these sites differ (CH_4 on a four-coordinate Pt atom is 0.29 eV higher in energy) but the calculated frequencies and relative intensities are rather similar, making it difficult to determine which site is favored.

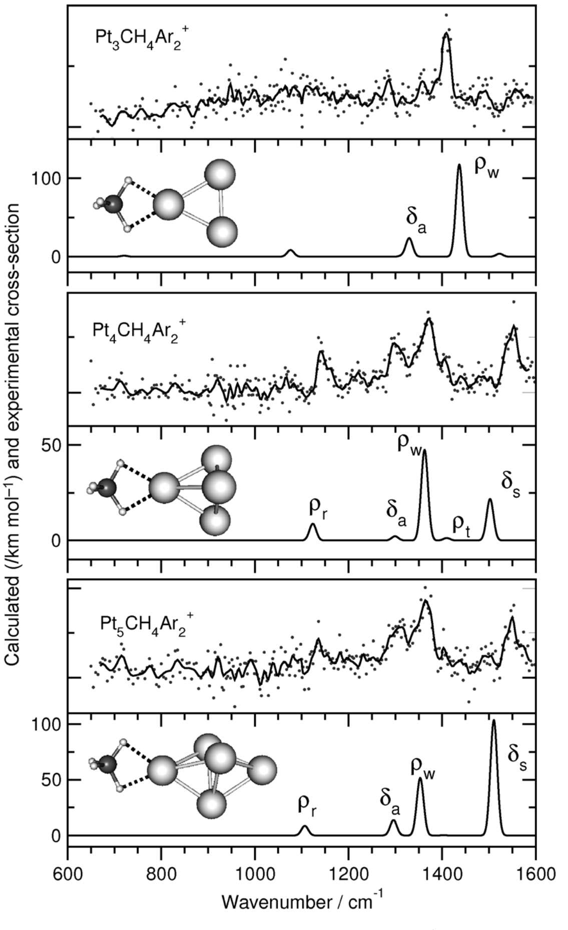

Figure 2. Experimental IR-MPD spectra of $Pt_nCH_4Ar_2^+$ ($n = 3$–5), monitored by depletion of the parent-ion signal in all cases. The most intense peaks correspond to a decrease of approximately 60% in the parent signal. The experimental data (gray points) are smoothed with a nine-point binomial average. The calculated structures and spectra, with assignments, that provide the best match to the experiment are shown for the $Pt_nCH_4^+$ complexes. The calculated vibrational frequencies are scaled by a factor of 0.97.

Overall, the agreement between theory and experiment is good for $n = 4,5$, matching the number, position, and relative intensities of the bands. The agreement for $Pt_3CH_4^+$ is less good than for the larger clusters, but a similar blue-shift of the intense ρ_w feature around 1400 cm^{-1} is observed in both the experimental and calculated spectra. The structures we identify are similar to those predicted for $Pt_3CH_4^+$[11] and $Pt_4CH_4^+$.[13]

To investigate the degree of activation of the C–H bonds in the complexes, we compared the changes of the C–H bond lengths with those of small hydrocarbons. The most activated, tertiary, C–H bond in isobutane has a bond length of 1.122 Å, while free CH_4 has a bond length of 1.087 Å, a change of the order of 0.03 Å.[24] The most activated bonds in the $n = 3,4,5$ complexes are calculated to be 1.15, 1.13, and 1.14 Å, respectively, while the "unactivated" bonds and free CH_4 are all 1.09 Å. Such elongation, of up to 0.06 Å, of the C–H bonds in the complex demonstrates that the methane is highly activated. For comparison, Öström et al.[5] found the η_1-CH_4 on Pt(977) to have a bond length of 1.18 ± 0.05 Å. The Pt–CH_4 binding fits into the picture of an agostic bond, with interaction between a filled C–H sp^3 orbital and a Pt d orbital.[13,14,25]

The dissociation channels for the different cluster sizes after IR excitation can also provide useful information. Figure 3 shows the changes in mass-spectral intensity for the important species involved in the IRMPD process for $n = 4,5$. For the $Pt_{3,5}^+$ complexes, we observe growth (corresponding to the depletion of the Ar complexes) primarily in the $Pt_{3,5}CH_2^+$ and $Pt_{3,5}CH_4^+$ channels, showing that the IR excitation can drive the partial dehydrogenation reaction in competition with dissociation by loss of Ar or CH_4. In contrast, for Pt_4^+, growth in the $Pt_4CH_2^+$ channel is not observed, indicating that the rate of IR-induced dehydrogenation is lower than the rates of Ar or CH_4 boil-off. This low observed reactivity of Pt_4^+ is consistent with previous studies[8–10] but suggests that, along with the lack of thermodynamic driving force reported by Koszinowski et al.,[9] there may also be a larger barrier to partial dehydrogenation on Pt_4^+ than on the other cluster sizes. The suggestion that the barrier to dehydrogenation on Pt_4^+ is higher than that for CH_4

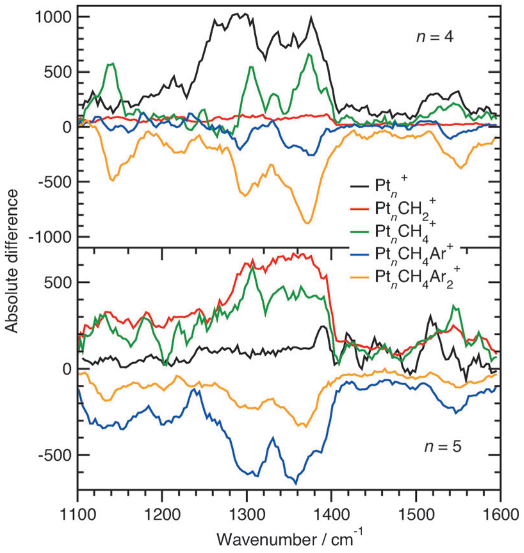

Figure 3. Absolute differences in mass-spectrometric intensity following IR-MPD for four- and five-atom Pt clusters.

desorption is consistent with the calculations of Lv et al.,[13] who reported the transition state (TS) for Pt_4^+ insertion into a C−H bond to be higher in energy than the separated species, in contrast to Pt_3^+, where this TS lies slightly lower in energy than the separated molecules. Entropic factors may also be important, given that the number of pathways for dissociation are presumably much greater than for dehydrogenation.

The structures we have identified for methane adsorbed on small clusters have different binding geometries to those identified on extended platinum surfaces.[5] Despite this, the dehydrogenation reaction pathways appear to be similar, and our findings support the model of De Witt et al. in which dissociative adsorption of methane on Pt proceeds via a shallow minimum with similar barriers to dehydrogenation and desorption.[2] The experimental dissociation channels and calculated C−H bond activation correlate well with the results of previous FT-ICR reactivity studies, with Pt_4^+ showing less overall reactivity and much lower activity for dehydrogenation. The observation that the C−H bond activation is distributed over two bonds on the cluster, with a corresponding reduction in the degree of activation of each bond may explain the previously noted reduced activity of supported Pt nanoclusters compared to extended Pt surfaces.[2] This reduced activation may, however, be an advantage, allowing greater control over the reactivity of methane on nanostructured catalysts.

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