# UV Raman Spectrum of 1,3-Dimethylcyclopentenyl Cation Adsorbed in Zeolite H-MFI

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Since its discovery in the early 1970s, the methanol-to-gasoline (MTG) conversion over zeolite H-MFI (also called HZSM-5), HSAPO-34, and other solid acid catalysts has attracted tremendous attention from both the academic and industrial research communities.[1−3] In this reaction, the kinetic induction period that precedes large-scale hydrocarbon production motivated reports from the groups of Kolboe[4−7] and Haw[8−13] that support a "hydrocarbon pool" mechanism for this reaction. Using NMR spectroscopy, theoretical calculations, and other methods Haw and co-workers have specified constituents of the hydrocarbon pool. Aromatic hydrocarbons, especially methylbenzenes, are active on many catalysts.[10] On H-MFI the hydrocarbon pool also includes the 1,3-dimethylcyclopentenyl cation **1** in equilibrium with the neutral cyclic diene **2**.
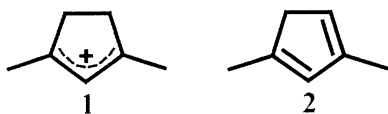
Haw and co-workers synthesized cation **1** in zeolite H-MFI by pulsing ethylene-$^{13}C_2$ onto the catalyst in a flow reactor at 623 K and then rapidly quenching the temperature to ambient. Solid-state NMR showed that cation **1** was the predominant organic species in the catalyst. The stability of the ion pair of **1** and the conjugate base of the zeolite was confirmed by theoretical calculations, which also established the stability of the $\pi$ complex of **2** and the zeolite acid site as a state only 2.2 kcal/mol higher in energy than the ion pair.

The vibrational spectrum of cation **1** has not been reported previously, either as the free molecule in solution or adsorbed on a solid. Recently ultraviolet Raman spectroscopy has been shown to be a powerful method for the identification of molecular species adsorbed in zeolites. We present in this report the first Raman spectrum of **1** adsorbed in a zeolite. We believe this to be the first Raman spectrum of an adsorbed carbenium ion.

Zeolite H-MFI (Si/Al =14) with several percent of the acid sites exchanged with cation **1** was prepared as before[9] and the sample was checked by $^{13}C$ MAS NMR. The UV Raman spectrum of this sample (Figure 1) was then measured at 298 K using a fluidized bed[14] in flowing helium to minimize both laser-induced decomposition and contributions from the products of decomposition to the spectrum; 2 mW of laser power and an 1800 s collection time were used for this measurement. The signal-to-noise of the spectrum is limited by the low loading of **1** in the zeolite matrix. The number of **1** cations in the volume sampled by the Raman spectrometer is

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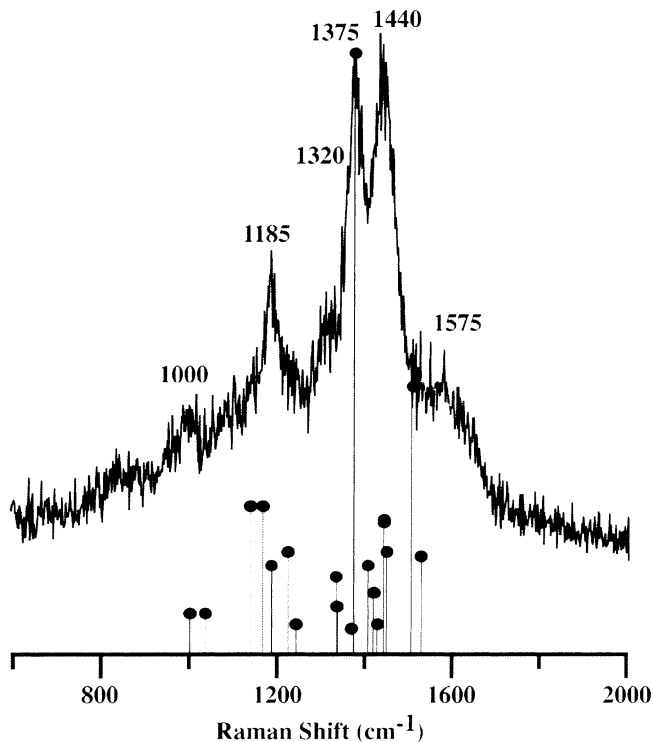
**Figure 1.** Experimental UV Raman spectrum (curve) and calculated normal Raman spectrum (vertical lines) of the 1,3-dimethylcyclopentenyl carbenium ion (cation **1**) in zeolite H-MFI.

estimated from the yield and acid site density to be at most $6 \times 10^{12}$ molecules. The equivalent solution-phase concentration would be $8 \times 10^{-5}$ M.

We attribute our ability to detect cation **1** at such low concentrations to resonance enhancement of the Raman intensity produced by UV excitation. The Raman spectrum shows prominent peaks at 1185, 1375, and 1440 cm$^{-1}$ and smaller peaks at 1000, 1320, and 1575 cm$^{-1}$.

The assignment of Raman bands from cation **1** was performed by optimizing the geometry[15] of cation **1** using density functional theory[16] (DFT) at the B3LYP/6-311G* level,[17,18] and then calculating the Raman frequencies and intensities analytically. Calculated Raman shifts were multiplied by the well-established scaling factor of 0.98[19] to match the Raman band at 1375 cm$^{-1}$. Such scale factors are commonly used to account for the effects of anharmonicity, missing from the harmonic frequency calculation done here.

Table 1 gives the vibrational band assignments, and the experimental and calculated Raman shifts for peaks with significant intensity in the Raman spectrum. The close correspondence between

***Table 1.*** Cation 1 Raman Band Assignments and Raman Shifts from Experiment and Theoretical Calculations

| Raman band assignments[a] | Raman shifts from experiment (cm$^{-1}$) | calculated Raman shifts (cm$^{-1}$) |
|---|---|---|
| CH$_3$, CH$_2$ rock | 1000 | 1024 |
| CH$_2$ H−C−C asym bend | 1185 | 1187 |
| CH$_2$ H−C−C bend | ∼1240 | 1225 |
| | (A shoulder of 1185) | |
| CH$_3$, CH$_2$ H−C−C bend | 1320 | 1333 |
| CH$_3$ H−C−H sym bend | 1375 | 1375 |
| H−C−H & H−C−C oop bend | 1440 | 1442 |
| CH$_3$ H−C−C in-plane bend | ∼1510 | 1507 |
| | (A shoulder of 1440) | |
| CH$_3$, CH$_2$ & CH H−C−C bend | 1575 | 1527 |

[a] Note: oop = out of plane; sym = symmetric; asym = anti-symmetric.

the calculated and measured Raman shifts is consistent with the NMR identification of the adsorbed species as cation **1**. The measured and computed intensities are not expected to match since the former is resonance-enhanced. The fact that the computed band positions, which correspond to the isolated cation, are so similar to the molecule residing in the pores of H-MFI signifies that the cation is little perturbed by interaction with the pore walls. This is also evident in recently published comparisons between UV Raman spectra of adsorbed and neat hydrocarbons.[14] On the basis of the close correspondence between FT-Raman spectra of hydrocarbons adsorbed in the all-silica form of zeolite MFI, which has no acidity, and solution-phase data, it is not surprising that UV Raman spectra of neutral hydrocarbons are essentially unchanged on adsorption.[20,21] That this correspondence carries over to carbenium ions that interact with anions in the zeolite framework is remarkable. This result, in general, suggests that UV Raman spectra of solution-phase species should be useful for the identification of these species within zeolite pores.

Interestingly, in situ UV Raman measurements carried out in our laboratory to characterize the adsorbed hydrocarbon species produced during methanol conversion catalysis at 543 K do not show evidence for cation **1**.[22] Instead, we observe a neutral cyclopentadiene very similar to species **2**, which Haw and co-workers predicted to be very slightly less stable than the ion pair of **1** and the zeolite conjugate base. It may be that the relative stabilities of the ion pair of **1** and the $\pi$ complex of **2** in the zeolite cross over between room temperature (NMR measurement) and 543 K (Raman measurement). If so, additional Raman studies

carried out over a range of temperatures and reaction conditions may be able to elucidate further details of this interesting reaction. Alternatively, there is also a significant difference in the Si/Al ratio for the H-MFI zeolites used in ours and Haw's laboratories, 90 and 14, respectively. Thus, the expected, lower concentration of cation **1** in our H-MFI zeolite would be below the detection limit.

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