for J(Si–Si) in both the disilene and 1,3-disiloxane systems provide experimental verification for the proposed bonding descriptions.

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Inelastic Neutron Scattering from Tetramethylammonium Cations Occluded within Zeolites

T. O. Brun,* L. A. Curtiss, L. E. Iton, and R. Kleb

Materials Science Division,[†] *Argonne National Laboratory*
Argonne, Illinois 60521

J. M. Newsam,* R. A. Beyerlein, and D. E. W. Vaughan

Exxon Research and Engineering Company
Annandale, New Jersey 08801

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The use of organic bases, for example, tetraalkylammonium hydroxides, and other organic reagents has greatly enhanced the scope of gel/solution synthesis routes to crystalline microporous materials such as zeolites.[1,2] The role of these organic components, however, continues to be the topic of considerable debate. The organic components first modify the gel structural chemistry. The presence of tetramethylammonium (TMA) hydroxide, for example, promotes the formation of double four-ring units in silicate solutions.[3,4] Occlusion of organic gel components in zeolite crystal structures, however, leads also to the concept of a "templating" effect[5] in which the organic component provides a basis around which the developing zeolite cages form. The mechanism of this templating process remains somewhat ill defined and must, at least, be of variable specificity. Thus a wide range of organic amines can be used to precipitate formation of ALPO-5 (AFI framework),[6] whereas in other systems such as TPA-ZSM-5 (MFI)[7] and SAPO-37 (FAU)[8] there appears to be a close correspondence between the conformation and/or amount of template(s) and the size, shape, and number of channel intersections or cages in the zeolite crystal structure. The occluded templates have been studied by powder X-ray diffraction,[9] ^{13}C NMR,[10,11] and Raman spectroscopy.[12,13] We describe here the use of inelastic neutron scattering (INS) to measure TMA template torsional vibrations, vibrations that prove to be sensitive to the strength of the interaction between the template cation and the enclosing zeolite cage.

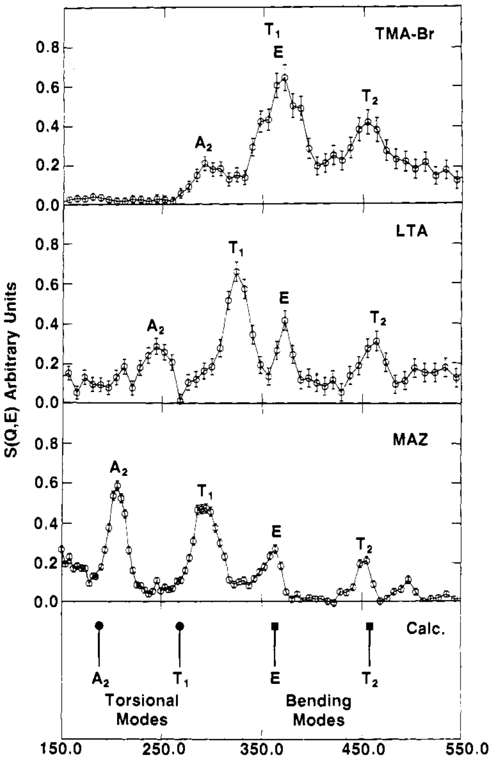

Figure 1. Inelastic neutron scattering spectra (energy loss mode) for TMA cations in TMA-Br (16 K, CAS, top), zeolite ZK-4 (14 K, CAS, middle), and zeolite omega (12 K, QENS, bottom). The assignments of the torsion and bending modes are shown. The bottom vertical lines indicate the scaled torsion and bending mode frequencies from the ab initio calculation for the free ion.

Table I. Torsion and Bending Mode Frequencies (cm^{-1}) for Tetramethylammonium (TMA) Cations in Various Environments

	torsion		bending		
environment	singlet A_2	triplet T_1	doublet E	triplet T_2	ref
TMA-Cl	301		371	456	17
TMA-Br	294	363		456	17
TMA-Br	290	370		455	this work (CAS)
TMA-I	265	344		451	17
LTA	245	325	372	460	this work (CAS)
MAZ	206	293	365	454	this work (QENS)
TMA (soln)			370	455	13
TMA (free ion calcd)	199	287	385	485	this work

Samples of zeolites ZK-4 (LTA) and omega (MAZ) of respective compositions $Na_{9.66}TMA_{0.96}Al_{10.62}Si_{13.38}O_{48}\cdot nH_2O$ and $Na_{6.93}TMA_{1.92}Al_{8.85}Si_{27.15}O_{72}\cdot mH_2O$ were prepared by using literature procedures[14,15] and characterized by inductively coupled plasma emission spectroscopy (ICPES), powder X-ray diffraction, ^{29}Si NMR, and thermogravimetric analysis (TGA). The samples were dehydrated under flowing Ar at 350 (LTA) and 400 °C (MAZ), respectively, for 2 h and loaded into 0.005-in.-walled, $^{7}/_{16}$-in. outside diameter vanadium sample cans fitted with vacuum-tight end caps. The INS spectra were recorded at 14 K on the CAS (LTA) and at 12 K on the QENS (MAZ) spectrometers

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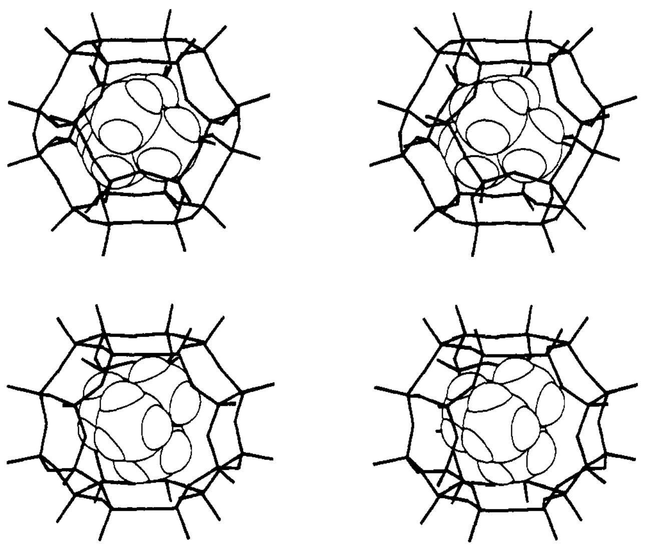

Figure 2. Stereopair representations of a TMA cation in a sodalite cage (upper) and in a gmelinite cage (lower) generated by using interactive molecular graphics. The aluminosilicate cages are represented as straight lines connecting bonded atoms (Si/Al and O). The orientation of the TMA cation in the sodalite cage is taken from ref 9. Drawing radii are C 1.77 Å, H 1.17 Å.

at the pulsed neutron source IPNS-I of Argonne National Laboratory.[16] (Both CAS and QENS are inverted-geometry spectrometers and spectra are measured in neutron energy loss mode.[17] The instrumental resolutions, $\Delta E/E$, for CAS and QENS are 0.03 and 0.015 respectively.) Selected regions of the INS spectra for the two materials are compared with that of TMA-Br (recorded at 16 K on CAS) in Figure 1. The frequencies of the modes displayed in Figure 1 are compared with those observed in the halide salts[18] in Table I.

The results of an ab initio molecular orbital calculation for an isolated TMA cation are also included in Table I. From the STO-3G basis set,[19] the vibrational frequencies of the free ion were determined from its harmonic force field calculated by analytical evaluation of the second derivatives of the Hartree–Fock energy with respect to the nuclear coordinates.[20] The STO-3G equilibrium structure of the TMA cation with tetrahedral symmetry [R(C–N) = 1.527 Å, R(C–H) = 1.089 Å, $\angle$H–C–H = 110.4°] was used in the calculation. The STO-3G predictions for the torsional and bending harmonic frequencies in Table I are expected to be reasonably accurate based on comparison of STO-3G[21] and experimental[22] vibrational frequencies for a related molecule, trimethylamine. For trimethylamine, the two STO-3G torsional frequencies are about 3% higher than the observed gas-phase torsional frequencies, while the two bending frequencies are about 10% higher. Hence, the theoretical results indicate that the torsional frequencies of the TMA ion in the gmelinite cage of zeolite omega are approaching those of the free ion. This is illustrated in Figure 1 where the theoretical torsional and bending frequencies are indicated, all scaled downward by 6% so that the experimental and theoretical bending modes approximately match (the theoretical frequencies in Table I are unscaled).

Consistent with earlier Raman results,[13] the bending modes vary little in energy from one material to another. The splitting between the two torsional modes is also fairly constant and in good agreement with the theoretical calculation. The positions of the torsional modes, that importantly are Raman inactive, however, are clearly very sensitive to the nature of the TMA environment. The marked frequency lowering (compared to the halide salts) for both torsional modes that occurs when the TMA cations are occluded in sodalite (LTA) or gmelinite (MAZ) cages (Figure 2) reveals that the interactions between the TMA cations and the zeolites are much weaker than those between TMA and the halide ions. Preliminary observation by INS of rotational diffusion of TMA at room temperature in both ZK-4 and omega samples is also consistent with weak TMA-zeolite interaction. The torsional frequencies are lower for the TMA ion in the gmelinite cage than in the slightly smaller sodalite cage. The isolated TMA ion represents a cage of infinite dimension, and its torsional frequencies are lower still. This general trend parallels the trend in ^{13}C NMR chemical shifts with cage size,[10,11] although the results of a broader series of measurements (currently under way) are required in order to quantify the relative importance of direct cage size effects and framework composition or nonframework cation influences.

The lack of selection rules and the very high sensitivity to modes involving hydrogen atom motion make inelastic neutron scattering a very useful probe of the dynamics, particularly the torsional modes, of organic species occluded within zeolites. It will be interesting to extend the present studies to INS measurements both of TMA cations during the process of zeolite crystallization and of TMA ions in cages larger than the gmelinite cage in order to probe further the approach of the torsional frequencies to the free ion values.

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Molecular Recognition: New Shapes for Asymmetric Microenvironments

Julius Rebek, Jr.,* Ben Askew, Pablo Ballester, and
Maria Doa

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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Asymmetric synthesis is a widely pursued goal in modern organic chemistry. A number of systems which feature C_2 symmetry elements in their ligands, such as Sharpless' epoxidation reagent,[1] Noyori's catalysts,[2] and Masamune's boranes,[3] are so successful that there is much confidence placed in the use of such symmetry elements in reagent and catalyst design.[4] This shape may be well suited for distinguishing between the two faces of a π system, but it is not obvious that C_2 symmetry offers advantages or is even appropriate for the recognition of single asymmetric centers. Whether such recognition involves minimizing steric effects involving large, medium, and small groups (eq. 1) or maximizing donor (D) and acceptor (A) attractions (eq 2) between substrate and receptor, *three* domains appear to offer a better fit than the *two* inherent in structures of C_2 symmetry. Accordingly, we have prepared structures in which three groups are spatially arranged in the desired sense.

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