Intrazeolite Phototopaxy: EXAFS Analysis of Precursor $8\{W(CO)\}_6\}^+\text{Na}_{48}Y$ and Photooxidation Products $16(WO_3)^+\text{Na}_{48}Y$ and $28(WO_3)^+\text{Na}_{48}Y$

Karina Moller,* Thomas Bein,
Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Saim Özkar,† and Geoffrey A. Ozin‡
Lash Miller Chemistry Department, University of Toronto, Toronto, Ontario, Canada M5S 1A1
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The intrazeolite photooxidation chemistry of α-cage encapsulated hexacarbonyltungsten(0) in Na$_{48}$Y with O$_2$, denoted nW(CO)$_6$Na$_{48}$Y/O$_2$/hv, which has previously been shown to provide a novel synthetic pathway to α-cage located tungsten(VI) oxide, denoted n(WO$_3$)Na$_{48}$Y, is now the subject of an extended X-ray absorption fine structure (EXAFS) analysis. The EXAFS data of a precursor $8\{W(CO)\}_6\}^+\text{Na}_{48}Y$, which contains on average one W(CO)$_6$ per α-cage shows that the W(CO)$_6$ guest maintains its structural integrity with only minor observable perturbations of the skeletal WC and ligand CO bonds compared to those found for the same molecule in the free state. The EXAFS analysis results for the photooxidation products 16(WO$_3$)-Na$_{48}$Y and 28(WO$_3$)-Na$_{48}$Y are very similar and display the presence of two terminal tungsten−oxygen bonds (1.75−1.77 Å) and two bridging tungsten−oxide bonds (1.94−1.95 Å), together with a short distance to a second tungsten (3.24−3.30 Å). This bond length and coordination number information for $n=16$ and 28 samples is best interpreted in terms of the formation of a single kind of tungsten trioxide dimer unit (WO$_3$)$_2$, most likely interacting with extraframework Na$^+$ cations, denoted ZONa$^+$O$_2$W(μ-O$_2$)WO$_2$NaOZ. In conjunction with earlier chemical and spectroscopic information on this system, the EXAFS data support the contention that 16(WO$_3$)-Na$_{48}$Y contains a uniform array of single size and shape tungsten(VI) oxide dimers (WO$_3$)$_2$ housed in the 13-Å supercages of the zeolite Y host. The sequential addition of WO$_3$ units to the 16(WO$_3$)-Na$_{48}$Y sample appears to increase the (WO$_3$)$_2$ dimer population, causing a buildup of α-cage encapsulated dimers-of-dimers [(WO$_3$)$_2$]$_2$ rather than further cluster growth to trimers (WO$_3$)$_2$ and/or tetramers (WO$_3$)$_4$.

Introduction

Metal organic chemical vapor deposition (MOCVD) has proven to have enormous technological importance in the epitaxial and photopetaxial production of thin films and low dimensional quantum nanostuctures for use in electronic and optical devices. Thermal MOCVD has only very recently been used for the synthesis of intrazeolite quantum supralattices which are of great current interest for future applications in quantum electronic and nonlinear optical devices.

We recently demonstrated that the photooxidation of α-cage encapsulated hexacarbonyltungsten(0), nW(CO)$_6$Na$_{48}$Y, provides a mild, clean, and quantitative synthetic pathway to α-cage encapsulated, single-size tungsten(VI) oxide clusters n(WO$_3$)-Na$_{48}$Y according to the reaction scheme

$nW(CO)_6Na_{48}Y + \frac{3}{2}nO_2 \rightarrow n(WO_3)-Na_{48}Y + 6nCO_2$

We like to refer to this kind of three-dimensional surface, host-guest inclusion chemistry as "intrazeolite metal carbonyl photopaxy" to bring forth the resemblance to a similar type of photocopy chemistry performed on a two-dimensional surface known as photopatography.

This type of intrazeolite W(CO)$_6$ photooxidation chemistry was anticipated to proceed cleanly to zeolite Y encapsulated WO$_3$ aggregates, based on precedents in the organometallic and matrix isolation literature exemplified by the following rhenium(I) and molybdenum(0) systems:

$R(CO)_6 \text{Ar, I, O}$

In the case of the precursor nW(CO)$_6$Na$_{48}$Y, the key points that have emerged from the chemical and spectroscopic studies include the following: (i) the hexacarbonyltungsten(0) molecule appears to be associated with two α-cage extraframework Na$^+$ cations (or Bronsted protons for H$_2$Y as host), via the oxygen end of two trans-bonded carbonyl ligands with saturation loading of two W(CO)$_6$ per α-cage; (ii) the hexacarbonyltungsten(0) guest is confined to the internal surface of the zeolite Y host with a homogeneous distribution throughout the zeolite crystals.

With respect to the product n(WO$_3$)-Na$_{48}$Y, it has been discovered that a sequential saturation loading/photooxidation scheme of the type laid out below satisfactorily accounts for the chemistry and spectroscopy of the system:

$16W(CO)_6-\text{Na}_{48}Y(\text{H}_2Y) \rightarrow 16WO_3-\text{Na}_{48}Y(\text{H}_2Y) \rightarrow 8WO_3-\text{Na}_{48}Y(\text{H}_2Y)$

$28W(CO)_6-\text{Na}_{48}Y(\text{H}_2Y) \rightarrow 24WO_3-\text{Na}_{48}Y(\text{H}_2Y) \rightarrow 28WO_3-\text{Na}_{48}Y(\text{H}_2Y)$

By employing the above impregnation method, it proved possible to organize the intrazeolite tungsten(VI) oxide system from one containing what was believed at the time to be isolated (uncoupled) α-cage encapsulated (WO$_3$)$_2$ dimers at n < 8, to a quantum

On sabbatical leave from the Chemistry Department, Middle East Technical University, Ankara, Turkey.

References cited therein:


supralattice built of coupled (WO₃)₂ dimers at n = 16, all the way to a quantum supralattice of coupled (WO₃)₂ or (WO₃)₄ units at n = 32. With the data available in the loading range 16 < n ≤ 32, it did not prove possible to differentiate between the di-mer-of-dimers and tetramer α-cage encapsulation models for n(WO₃)₅-NaₓY. A kind of connectivity or percolation threshold appears to occur around n ≈ 8 as was signaled by a red shift on the absorption edge of n(WO₃)₅-NaₓY and provides some evidence for intercavity (α-cage) electronic coupling between (WO₃)₂ dimer units.

Evidence for local field effects arising from the presence of "half-naked" Na⁺ supercage cations (or protons for H₃Y) interacting with the oxygen end of the carbonyl ligands of the precursor W(CO)₆ and located at the "surface" of the product (WO₃)₅ dimer has been found in the observation of W(CO)₆ and (WO₃)₂ induced alterations in the frequencies of mid-IR ZOH, stretching modes and far-IR Na⁺ translatory modes, ¹³C, ²⁹Si, and ²³Na MAS-NMR chemical shifts, and W LIII XPS ionization potentials. By intentionally varying the ionic potential of the constituent supercage cations in the series 16(WO₃)₅-MₓY, where M = H, Li, Na, K, Rb, Cs, it has proven possible to "fine tune" the band-gap of the tungsten(VI) oxide quantum supralattice by as much as 0.75 eV.

In what follows we report EXAFS structure determinations for some key materials in the above story, namely, the precursor 8(W(CO)₆)₅-NaₓY and photooxidation products 16(WO₃)₅-NaₓY and 28(WO₃)₅-NaₓY.

Experimental Section

The precursor sample denoted 8(W(CO)₆)₅-NaₓY and first and third stage photooxidation products (see above sequential saturation loading/photooxidation scheme) denoted 16(WO₃)₅-NaₓY and 28(WO₃)₅-NaₓY were prepared according to the procedures described previously.

Data acquisition was carried out at the National Synchrotron Light Source at Brookhaven National Laboratories with a stored electron energy of 2.5 GeV and ring currents between 90 and 170 mA. The WLIII edge (10 207 eV) X-ray absorption data were collected on beamline X-11A and X-19A with a Si(111) crystal pair monochromator.

Measurements were performed in transmission at liquid nitrogen temperature. EXAFS samples were prepared such as to give a total absorption of about \( p_x = 2.0 \) (\( p \) = absorption coefficient, \( x \) = sample thickness) and an absorption step of about 1.0 at the edge to obtain an optical signal-to-noise ratio. Zeolite powder was embedded in an octadecane/eicosane mixture and kept under a nitrogen atmosphere until data collection. Air stable compounds were finely ground and mixed with BN to give a self-supporting pellet.

The EXAFS data were analyzed following standard procedures using a software package provided by D. C. Koningsberger. Background removal was accomplished by applying a Victoreen fit to the preedge region and a cubic spline function to the EXAFS data, the latter being fine-tuned by a smoothing parameter. Normalization to a per atom basis was performed by dividing the

Figure 1. k¹-weighted Fourier transformation (k = 3-16 Å⁻¹) of (a) W(CO)₆ reference and (b) sample 8(W(CO)₆)₅-NaₓY. (b and c) Back-transformations of (c) first shell (0-2.0 Å) and (d) second shell (2.0-3.3 Å) of sample 8(W(CO)₆)₅-NaₓY; original data (solid line) and fit (broken line).

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EXAFS spectrum by the height of the absorption edge which is proportional to the total number of absorbing atoms. The fitting procedure is based upon the plane-wave approximation using a least-squares routine. Phase functions and backscattering amplitudes used in the fitting procedure were extracted from reference compounds (Table I).

Results

Precursor Sample: \(8[(\text{W(CO)}_6)\text{Na}_8]_Y\). Hexacarbonyltungsten(0) adsorbed from the vapor phase into vacuum thermally dehydrated zeolite \(\text{Na}_8\text{Y}\) served as the precursor for the photooxidative synthesis of tungsten oxide clusters. EXAFS measurements were performed with a sample loaded with eight \(\text{W(CO)}_6\) molecules per unit cell (that is, one \(\text{W(CO)}_6\) per \(\alpha\)-cage), denoted \(8[(\text{W(CO)}_6)\text{Na}_8]_Y\), as well as on neat \(\text{W(CO)}_6\). After background subtraction and normalization, a Fourier transformation was applied to the data, weighed by \(k^4\), resulting in a radial distribution function of atoms surrounding the tungsten absorber. Spectra for (a) \(\text{W(CO)}_6\) and (b) \(8[(\text{W(CO)}_6)\text{Na}_8]_Y\) are shown in Figure 1. At this stage of the analysis, peak positions give only approximate bond distances, due to an element-specific phase shift. Accurate values are obtained by fitting with adequate reference compounds.

A qualitative comparison between parts a and b of Figure 1 immediately reveals a strong similarity between pure \(\text{W(CO)}_6\) and that same compound adsorbed in the zeolite. A fit was performed separately on the W-C_ and W-CQ ligand sphere of sample 8 (\(\text{W(CO)}_6\))_Y with the reference \(\text{W(CO)}_6\). The back-transformed individual carbon and oxygen shells are shown in Figure 1c,d where they are overlayed with the fitting result. The resulting coordination numbers of 6.5 and 6.8 and bond distances of 2.06 and 3.21 Å, respectively, are within the limits of accuracy, identical with the reference compound \(\text{W(CO)}_6\) (see Tables I and II).

First Stage Saturation Loading/Photooxidation Product: \(16(\text{WO}_3)\text{Na}_8\) \(Y\). A Fourier transformation similar to the precursor \(8[(\text{W(CO)}_6)\text{Na}_8]_Y\) was performed on the photooxidation product \(16(\text{WO}_3)\text{Na}_8\) \(Y\) and is shown in Figure 2a. The latter was synthesized by \(\lambda > 240\) nm xenon lamp, room-temperature photolysis of \(16(\text{W(CO)}_6)\text{Na}_8\) \(Y\) using 400 Torr of dry \(\text{O}_2\). The dramatic structural changes that have occurred on oxidation are best visible in Figure 2b, where the magnitudes of the Fourier transformation of precursor sample \(8[(\text{W(CO)}_6)\text{Na}_8]_Y\) and product sample \(16(\text{WO}_3)\text{Na}_8\) \(Y\) are overlayed. A strong reduction in the W-C and W-CO coordination signals the loss of the carbonyl ligands. Simultaneously, a new peak at much shorter distances is visible at about 1.3 Å (uncorrected for phase shift). As the intrazeolite photoproduct has been shown to be tung-
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The first shells \( W_2 \) and \( V_1 \) the bulk monoclinic form of \( W_0 \) was also fit results are somewhat comparable, but the back-transformation of these second modulation in its EXAFS spectrum (broken line), while coordination of \( W_0 \), is shown in Figure 3a. The smooth decay of the oscillation is characteristic for the presence of only one bond distance to the absorber atom. In contrast, the complex amplitude function of sample 16(WO3)-Na5Y when back-transformed indicates more than one nearest-neighbor distance as observed in Figure 2a, a smaller contribution at ca. 3.1 \( \AA \) occurs in the Fourier transformation. This peak is again different to that in bulk WO3, which has several \( W-W \) distances at ca. 3.7 \( \AA \). To evaluate this contribution, a \( k^2 \)-weighed Fourier transformation was applied to sample 16(WO3)-Na5Y, which will enhance the magnitude of scattering when heavy backscatters are present. The resulting spectrum is shown in Figure 4b. Clearly, the peak at 3.1 \( \AA \) has grown in intensity and is accompanied by side lobes (compare to Figure 2a). The signature of back-transformed peaks from the real space data is indicative for the nature of the respective ligand, and a number of such transformations with different windows were applied to this outer contribution. An example is shown in Figure 4d. The observed second maximum at \( k = 12 \) \( \AA^{-1} \) in the EXAFS modulation is a strong indication for the presence of a heavy scatterer such as tungsten. Other elements present in this sample like sodium or silicon cannot be responsible for this maximum at ca. 12 \( \AA^{-1} \) since their amplitude functions fall off rapidly at higher \( k \) values. However, they do seem to be convoluted in this peak, giving rise to the strong contribution between 2 and 6 \( \AA^{-1} \). The data analysis of this complex function was approached by fitting only the range between 6 and 14 \( \AA^{-1} \) in Figure 4-d, thereby discriminating any influence of light elements. Assuming that a \( W-O-W \) scatterer pair is predominant in this range, an adequate reference had to be found. The strong disorder in the second shell of WO3 excludes this oxide as a candidate, and the Re-O-Re shell of ReO3 was chosen instead. Its Fourier transformation and back-transformation are shown in Figure 4a,c. A fit performed with this reference resulted in a \( W-W \) bond length of 3.30 \( \AA \). In view of the\( W-W \) coordination number of 1.5 (see Table II). Inclusion of other scatterer pairs in the fit, e.g. \( W-Si \) atoms and \( W-Na \) did not give unique fit solutions. (Large static disorder was always observed.) However, the presence of a \( W-W \) scatterer pair could clearly be established. The obtained bond length of 3.30 \( \AA \) suggests a bent rather than a linear \( W-O-W \) structure. Doubly oxygen bridged tungsten(VI) centers have a bond distance of ca. 3.3 \( \AA \), while singly oxygen bridged ones are ca. 3.7 \( \AA \) apart.12

Third Stage Sequential Saturation Loading/Photooxidantation Product: 28(WO3)-Na5Y. The EXAFS data set and analysis results for the title sample proved to be remarkably similar to that described above for the first stage saturation loading/photooxidation product 16(WO3)-Na5Y (Table II). Using a similar fitting procedure for 28(WO3)-Na5Y as used for 16(WO3)-Na5Y, one again finds the presence of two different tungsten-oxygen distances, with a stable solution having a \( W-O \) bond at 1.75 \( \AA \) and a coordination number of 2.2 and a second \( W-O \) bond at 1.96 \( \AA \) with a coordination number of 2.2. The existence of a \( W-W \) scatterer pair was also clearly defined with a bond length of 3.24 \( \AA \) and a \( W-W \) coordination number of 1.4 (see Table II). From these results it would therefore appear that the sequential addition of WO3 units to the 16(WO3)-Na5Y sample simply enhances the (WO3)2 dimer population. In view of the fact that 16(WO3)-Na5Y already contains one (WO3)2 dimer motif per \( \alpha \)-cage, the further addition of WO3 units is envisaged as a continued buildup of \( \alpha \)-cage (WO3)2 dimers, resulting in an accumulation of \( \alpha \)-cage encapsulated dimers-of-dimers ([(WO3)2]2) rather than \( \alpha \)-cage cluster growth to trimers (WO3)3 and/or tetramers (WO4). The geometric and spatial feasibility of the favored \( \alpha \)-cage dimers-of-dimers ([(WO3)2]2) aggregate can be as-

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**Figure 3.** (a) Back-transformed first shell (0.0–1.9 \( \AA \)) of reference Na2WO3 and (b) of sample 16(WO3)-Na5Y (solid line), overlayed with fit results (broken line).

**Table II: Structural Data As Derived from EXAFS Analysis**

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<th>sample</th>
<th>atom pair</th>
<th>( N_0 )</th>
<th>( R/\AA )</th>
<th>( \Delta R/\AA )</th>
<th>( \Delta E/eV )</th>
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<td>8(W(CO)6)-Na5Y</td>
<td>W-CO</td>
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<td>0.0003</td>
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<td>W-O</td>
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<td>3.21</td>
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<td>28(WO3)-Na5Y</td>
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<td>0.0008</td>
<td>3.8</td>
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<tr>
<td>W-W</td>
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<td>0.0009</td>
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<tr>
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<td>0.0030</td>
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<tr>
<td>W-O</td>
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<td>3.15</td>
<td>0.0010</td>
<td>-3.9</td>
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<td>3.24</td>
<td>0.0016</td>
<td>4.3</td>
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*Coordination number. Bond distance. Static disorder. Inner potential.

As observed in Table II, the bulk monoclinic form of WO3 was also measured for comparison and is shown in Figure 2c. The first shells (0–2 \( \AA \)) of bulk WO3 and sample 16(WO3)-Na5Y are somewhat comparable, but the back-transformation of these contributions clearly shows a different ligand distribution in both compounds (see Figure 2d). WO3 shows a strong damping of the second modulation in its EXAFS spectrum (broken line), while 16(WO3)-Na5Y has a distinctive node at \( k = 8 \) \( \AA^{-1} \) (solid line) which may be attributed to the presence of two closely spaced ligand shells. (Monoclinic WO3 has a broad distribution of W-O bond lengths between 1.71 and 2.21 \( \AA \).) The complex amplitude function of 16(WO3)-Na5Y was analyzed by using a two-shell fit, which accounts for two different tungsten-oxygen distances, a stable solution was obtained with a \( W-O \) bond at 1.77 \( \AA \) and a coordination number of 2.2 and a second \( W-O \) bond at 1.94 \( \AA \) with a coordination number of 1.8. The final result is seen in Figure 3a, the original data (solid line) are overlayed with the fit (broken line). Comparison with crystallographic data of molybdenum(VI) or tungsten(VI) oxides shows that terminal metal-oxygen double bonds have bond lengths of ca. 1.7 \( \AA \), while doubly and triply bridged metal-oxygen bonds appear at ca. 1.9 and 2.3 \( \AA \), respectively.12

Hence, the fit result of 1.94 \( \AA \) points to the presence of support-coordinated or multinuclear tungsten(VI) oxide clusters.

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Figure 4. $k^2$-weighted Fourier transformation of (a) reference ReO$_3$ ($k = 3.5-18$ Å$^{-1}$) and (b) of sample 16(WO$_3$)$_2$-Na$_{32}$Y ($k = 2.8-14$ Å$^{-1}$). (c) Back-transformed Re-Re atom pair of ReO$_3$ (2.2-2.7 Å) and (d) back-transformed outer shell of sample 16(WO$_3$)$_2$-Na$_{32}$Y (2.7-3.5 Å, solid line) and fit (broken line).

Figure 5. Summary illustration of the structural data for the precursor 8[W(CO)$_6$]-Na$_{32}$Y and pure W(CO)$_6$ as derived from EXAFS. $N_{O}$ is the coordination number for W-CO, $N_C$ is the coordination number for W-CO, and numbers in parentheses are structural data for the precursor, W(CO)$_6$.

certained from a CHEM-X molecular graphics structural model for
two orthogonally configured, α-cage immobilized ZONa-α2W-
(μ-O)$_2$W-O$_2$-NaOZ moieties, involving adjacent Na$^+$ site II cation
six-ring anchoring sites (Figure 7).

Conclusions

The structural data for the precursor 8[W(CO)$_6$]-Na$_{32}$Y and
photooxidation products 16(WO$_3$)$_2$-Na$_{32}$Y and 28(WO$_3$)$_2$-Na$_{32}$Y
as derived from the present EXAFS study, when taken in combina-
tion with earlier chemical and spectroscopic from
these laboratories for related systems, allow one to arrive at
the conclusions illustrated in Figures 5-7. The central points
to emerge from this study are summarized below.

(i) W(CO)$_6$ maintains its structural integrity when housed in
the α-cage of Na$_{32}$Y with only minor perturbations of the skeletal
WC and ligand CO bonds compared to those found for the free
molecule (Figure 5). Similar results have recently been found
for 8[Mo(CO)$_6$]-Rb$_{32}$Y, where evidence for the interaction of the
Mo(CO)$_6$ guest with extraframework Rb$^+$ cations was determined
by a combination of molybdenum and rubidium edge EXAFS
data (Figure 5).

(ii) In the case of 16(WO$_3$)$_2$-Na$_{32}$Y, the presence of two ter-
mina! oxygens (1.77 Å) and two bridging oxygens (1.94 Å) per
tungsten, together with a short distance to a second tungsten (3.30

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Low-Frequency Single-Crystal Raman, Far-Infrared, and Inelastic Neutron Scattering
Studies of Acetanilide at Low Temperature

Clifford T. Johnston,* Stephen F. Agnew†, Juergen Eckert,‡ Llewellyn H. Jones,§ Basil I. Swanson,∥ and Clifford J. Unkefer∥

INC-4 and P-LANSCE, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Single-crystal Raman, far-infrared (far-IR), and inelastic neutron scattering (INS) spectra of acetanilide (ACN) in the low-frequency region (20-200 cm⁻¹) were obtained as a function of temperature. At 20 K, a total of 29 low-frequency Raman-active vibrational modes were resolved and assigned to a unique symmetry species. For comparison, a total of 23 far-IR bands were observed in the 20-200-cm⁻¹ region at 20 K. Factor group analysis of ACN predicts 24 Raman-active and 15 IR-active phonon bands. The greater-than-expected number of observed bands in the low-frequency region was assigned to the presence of low-frequency internal modes that exhibit anomalous frequency-shift and line-narrowing behavior upon cooling. The most striking change occurs in the B₁₂ (xy) polarization where a single band at 126 cm⁻¹ at 305 K splits into three distinct, well-resolved bands at 133, 142, and 152 cm⁻¹ at 20 K. INS spectra of ACN and its deuterated isotopomers demonstrate clearly that the 142-cm⁻¹ band corresponds to a methyl torsion. In addition, low-frequency bands at 104 and 189 cm⁻¹ were assigned to internal modes. In contrast to the phonon modes, the low-frequency internal modes all exhibit greater line broadening with temperature.

Introduction

The anomalous temperature dependence of the amide-I region of crystalline acetanilide (ACN) has received considerable attention recently. 1-13.26 In the amide-I region, crystalline ACN is characterized by two strong Raman-active amide-I bands at 1665 cm⁻¹ (A₉) and 1678 cm⁻¹ (B₉), and one IR-active band at 1665 cm⁻¹ at 300 K. When ACN is cooled, a new IR- and Raman-active band appears at 1650 cm⁻¹, which increases in

1 INC-4.
2 P-LANSCE.

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Registry No. W(CO)₆, 14040-11-0; WO₃, 1314-35-8.

Figure 7. CHEM-X model for two orthogonally oriented, a-cage immobilized ZONa-O₃W(μ-O)₃WO₃-NaOZ moieties, involving adjacent Na⁺ site II cation six-ring anchoring sites.

*Department of Soil Science, University of Florida, Gainesville, Florida 32611
†Labs of Acetanilide at Low Temperature