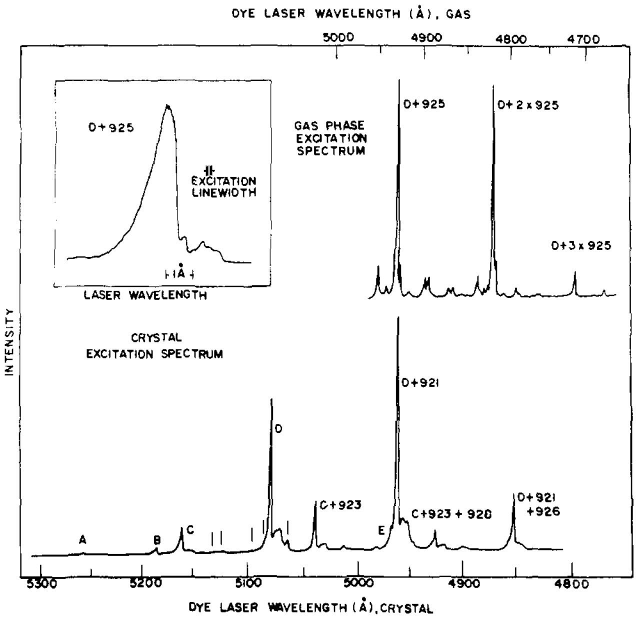

Figure 1. Two-photon spectra of benzene in the crystal and in the vapor: lower, the crystal excitation spectrum, the bands marked A through D are fundamentals of 177, 740, 922, and 1545 cm^{-1} respectively, and the progression forming mode is $a_g(1)$ at *ca.* 923 cm^{-1}; upper right, the vapor excitation spectrum at 70 Torr; upper left, a higher resolution spectrum of the vapor showing the asymmetry of the band caused by unresolved rotational structure.

focused into a cell containing the sample, and the sample luminescence detected by a sensitive photomultiplier is used to monitor the absorption. If the sample does not luminesce a signal can be generated by causing the sample excitation to be transferred (by collision or Förster transfer or energy migration in the solid) to a known energy acceptor which then luminesces. The dye-laser is constructed according to the Hänsch[2] design and is continuously tunable by means of a mechanical drive that rotates the diffraction grating which forms the rear reflector of the laser cavity. The laser line width which is controlled by the choice of cavity elements determines the spectral resolution. In the experiments we report here the laser line width was chosen to be *ca.* 2 cm^{-1} by placing a 10:1 beam expander in the cavity.

The method is useful for the study of liquids, dilute solutions, solids (*e.g.*, organic crystals), and gases. We previously reported[3] the two-photon allowed spectrum of the first singlet–singlet g → g transition of the biphenyl crystal, and this was the first high-resolution two-photon spectrum to be recorded. Using red to blue laser dyes we have now obtained high-resolution spectra of naphthalene (h_8 and d_8), naphthalene in durene, and benzene (h_6 and d_6) all at 2°K in single crystals. The benzene and naphthalene spectra refer to the lowest energy excited singlet states of these materials and they arise because of vibronic coupling through ungerade modes of the excited state since the overall selection rule for two-photon absorption (in the dipole–dipole approximation) is g $\rightleftarrows$ g, and these lowest excited states have u electronic symmetry. For the case of benzene we have observed an additional eight out of a total of ten ungerade fundamentals of the $^1B_{2u}$ state. The spectra of naphthalene and naphthalene in durene mixed crystals have been obtained with polarized light, and it is apparent that b_{1u} and b_{2u} (in-plane) vibrations of the first excited state are clearly distinguished as expected from a π-electron theory of two-photon absorption. It appears as if the two-photon spectrum of benzene is also consistent with a model in which the π electrons dominate the interactions of the molecule with the radiation. This technique has provided sufficient information to assign definitively a large number of excited state *u* vibrations for the first time.

We also wish to report our observation of two-photon absorption to vibronic levels of the $^1B_{2u}$ state of benzene vapor. The results, shown in Figure 1, open up the possibility of high-resolution gas-phase studies of molecules, exposing an entirely new set of upper states that have not been previously studied. The detailed rotational selection rules for these two-photon processes can be quite different from the conventional rules, even for diatomics, since among other things the angular momentum associated with the two-photons must be conserved. The benzene spectrum is two-photon forbidden (g → u) and requires a vibronic coupling, so we anticipate that allowed two-photon transitions should be readily observed in gases at low enough pressure to permit vibrational and rotational analyses, and single vibronic level excitation experiments.

Previous two-photon absorption studies involving a significant wavelength scan were done point by point at low resolution using high-powered single shot pulsed lasers to provide one of the photons[4–6] or have involved a single shot dye laser.[7]

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Crystal Structure of an Acetylene Sorption Complex of Partially Manganese(II)-Exchanged Zeolite A

Sir:

The catalytic and selective sorption properties of transition metal ion-exchanged zeolites are well known.[1] In such zeolites, it is observed that the amount and nature of the sorbate can greatly affect the coordination geometries about the transition metal ions. Using partially exchanged Co(II) and Ni(II) forms of the synthetic sieve zeolite 4A,[2] Klier has spectroscopically observed the formation of three-, four-, and six-coordinate Ni(II) and Co(II) complexes.[3,4] Recent X-ray diffraction studies have corroborated the existence of the

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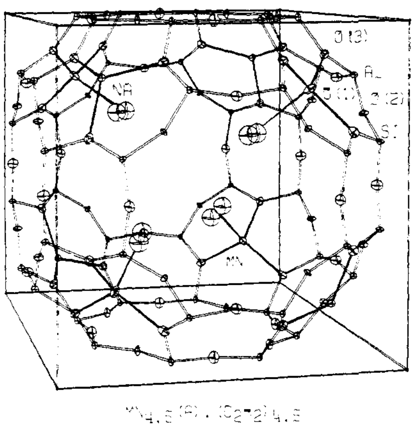

Figure 1. A view of the $Mn_{4.5}[A]\cdot(C_2H_2)_{4.5}$ unit cell is shown. Heavy bonds indicate the tetrahedral coordination about Mn(II); the trigonal coordination about Na^+ is indicated similarly. Ellipsoids of 10% probability are used: bond lengths in Å (Si,Al)-O (1) = 1.63 (2), (Si,Al)-O(2) = 1.65 (1), (Si,Al)-O(3) = 1.69 (1), Mn-O(3) = 2.17 (2), Mn-C = 2.61 (10), Na-O(3) = 2.18 (2), C-C = 0.7 (3); selected bond angles O(3)-Mn-O(3) = 115 (1)°, O(3)-Na-O(3) = 114(2)°.

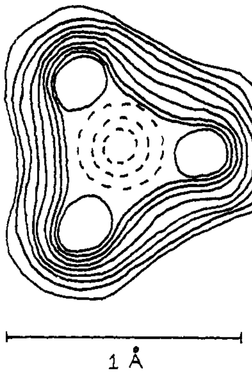

Figure 2. The electron density function in the plane normal to the threefold axis at x = 0.31, through the maximum of this peak. The contours are drawn at intervals of 0.1 e/Å^3, and the electron density maximum corresponds to 1.6 e/Å^3. Dashed contours at the center represent decreasing electron density. The standard deviation of the electron density is calculated to be 0.12 e/Å^3.

three-coordinate Co(II) species[5] and have demonstrated the presence of three- and five-coordinate Mn(II) intrazeolitic complexes.[6] As part of a continuing study of such transition metal complexes, the crystal structure of an acetylene sorption complex of a partially Mn(II) exchanged form of zeolite A is herein reported.

Crystals of sodium zeolite 4A (stoichiometry $Na_{12}Si_{12}Al_{12}O_{48}\cdot xH_2O$; $x \approx 27$) were prepared by the method of Charnell,[7] modified to include a second crystallization. Exchange with 0.1 M $Mn(ClO_4)_2\cdot 6H_2O$ was conducted at 28° for 3 months. Elemental analysis indicated the stoichiometry $Mn_{4.5}Na_3Si_{12}Al_{12}O_{48}\cdot xH_2O$, henceforth abbreviated $Mn_{4.5}[A]$ (water molecules excluded). The hydrated $Mn_{4.5}[A]$ crystals are light tan in color, possibly due to the formation of trace amounts of MnO_2.

One of the largest crystals, 0.070 mm along an edge, was placed in a thin-walled Pyrex capillary and affixed to a vacuum system. Total dehydration was achieved at a pressure of 1×10^{-6} Torr and a temperature of 350° in 48 hr. Once the crystal had returned to room temperature (23°), it was treated with 710 Torr of zeolitically dried acetylene. Then, under these conditions, the crystal in its capillary was removed from the vacuum line by torch. Microscopic examination of the crystal showed it to be yellow-orange in color.

This crystal was found to have cubic $Pm3m$ symmetry. (Reference 2b discusses the space group determination.) At 20 ± 1°, the unit cell constant is 12.205 (7) Å. All 870 unique reciprocal lattice points within the sphere defined by $2\theta < 70°$ were examined with Mo Kα radiation using a fully automated Syntex P$\bar{1}$ diffractometer. Experimental details and data reduction are as previously presented.[2b] The structure was solved and refined using those 208 reflections whose intensities exceeded three times their corresponding standard deviations. Full-matrix least-squares refinement,[8] using anisotropic thermal parameters for the zeolite framework atoms (Si, Al, O) and the Mn(II) ions, but isotropic thermal parameters for the Na^+ ions and the carbon atoms, converged at a conventional R value of 0.064 and a weighted R of 0.067.

Figure 1 is a view of the unit cell of the $Mn_{4.5}[A]$–acetylene sorption complex.[9] The Mn(II) ions and the Na^+ ions are located on the body diagonals of the unit cell, each bound to its own set of three oxygen atoms (O(3)'s), related by the threefold axes. The Mn^{II}–O(3) and the Na^+–O(3) bond lengths in the dehydrated $Mn_{4.5}[A]$ structure[6] (2.11 (1) and 2.16 (5) Å) and in the acetylene complex (2.17 (2) and 2.18 (2) Å) do not differ significantly. However, in order to accommodate a molecule of C_2H_2, each Mn(II) ion has moved substantially (0.60 Å) along the threefold axis, from just inside the sodalite unit in the dehydrated structure to a position in the large cavity. To more uniformly distribute positive charge, the Na^+ ions have moved from the large cavity into the sodalite units.

Some ambiguity, still largely unresolved, was encountered in the placement of the acetylene molecules. A three-dimensional difference Fourier function, prepared by substracting the fully refined atomic positions of all but the carbon atoms, indicated a broad torus of electron density (see Figure 2) centered at and orthogonal to the threefold axis. The maximum electron density through this torus is approximately 2.6 Å from the Mn(II) position. The distance to a Na^+ ion would be 4.4 Å, too long to be an interaction; accordingly, all of the C_2H_2 molecules represented by this torus are associated with Mn(II).

An attempt, partially successful, was made to decide whether the torus, clearly representing a disordered arrangement of acetylene molecules, could be resolved. The electron density function (Figure 2) argues strongly for a high degree of disorder, perhaps approaching entirely free rotation of C_2H_2 about an axis perpendicular to its molecular axis and coinciding with the threefold axis of the unit cell.

The position x, y, z was unstable with respect to x.

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(8) Principal computer programs used are: full-matrix least-squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317 (modified); Fourier program, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971; C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(9) See paragraph at end of paper regarding supplementary material.

x, z ($x < z$) in least-squares refinement. The positions x, x, z and x, z, z were refined together, each with an occupancy of 4.5 carbon atoms; this solution corresponds to three molecular sites, each centered about the threefold axis, but with nonequivalent carbon atoms in each molecule. Successful refinement yielded thermal parameters of 3 (3) Å^2 and 10 (4) Å^2, respectively, indicating again, although weakly, that the position x, x, z is a favored one.

Refinement with nine carbons at x, x, z converged with a thermal parameter of 10 (3) Å^2. The final R is equal to that of the structure described in the preceding paragraph. This solution corresponds to three molecular sites with equivalent carbon atoms; the molecular centers lie off the threefold axes and the C–C bonds are 0.7 (3) Å in length, too short to be correct but understandable as an aberration attributable to thermal motion foreshortening and the ancillary effects of generating three diatomic molecular sites from three atomic sites. The acetylene bond length in the gas is 1.201 (5) Å,[10] and in the C_2H_2 complex of zeolite 4A, the bonds are imprecisely determined (for the same reasons as discussed here): 1.03 (15) and 0.92 (10) Å.[11]

A final difference Fourier function indicated very broad peaks of height 0.8 (1) e Å^{-3} in the vicinity of the acetylene molecules; this is taken to indicate that the model of thermally isotropic carbon atoms on mirror planes is too simple, but that within that constraint this structure is correct. There is no crystallographic indication of the presence of additional acetylene molecules.

With nine carbon atoms at x, x, z, each carbon atom is 2.61 (10) Å from Mn(II). This distance is approximately independent of the choice of model. The interaction is therefore weak and apparently due to an electrostatic interaction between the dipositive Mn(II) ions and the polarizable π-electron density of the acetylene molecules. Since the manganese ions are dipositive, their d orbitals are contracted, and the synergistic bonding[12] between the metal and a weak σ-donor–strong π-acceptor such as acetylene is appreciably inhibited.

Although the uncertainty in the C–C bond is great, apparently no significant nonbonded approaches are made by acetylene to the zeolite framework. The closest such approach is 3.5 Å to an O(3) oxygen atom; the acetylenic hydrogens are therefore far from framework atoms as well.

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Supplementary Material Available. A listing of positional, thermal, and occupancy parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-8180.

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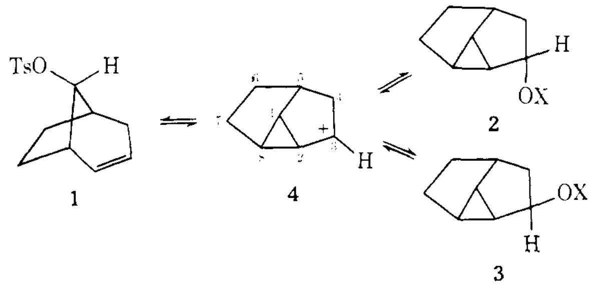
Experimental and Theoretical Evidence for Nonplanar Carbonium Ions. The Secondary Cyclopropylcarbinyl System

Sir:

Our studies of the solvolysis of *anti*-8-bicyclo[3.2.1]-oct-2-enyl *p*-toluenesulfonate (**1**)[1] and the epimeric *endo*- and *exo*-tricyclo[3.3.0.0^{2,8}]octan-3-yl derivatives (**2** and **3**) have strongly implicated the tricyclic cyclopropylcarbinyl cation **4** as the common product determining intermediate in these reactions. Controlled acetolysis and hydrolysis of **1**, **2**, and **3** give products having the bicyclo[3.3.0]oct-7-en-2-yl and bicyclo-[3.2.1]oct-2-en-8-yl (**1**) carbon skeletons in essentially constant proportions (~1.5–1.8), as well as acetates and alcohols having the tricyclic carbon skeleton of **2** and **3**. However, in each case the endo/exo product ratio of **2**/**3** was much greater than unity under kinetic control. For example, acetolysis of **1** (partial), **2**-OPNB, and **3**-OPNB at 76.1° showed values for **2**-OAc/**3**-OAc of >33, 14, and 3.3, respectively, whereas hydrolysis results (aqueous acetone or dioxane buffer) showed **2**-OH/**3**-OH ratios of 58, 48, and 40, respectively.[2] The relative rate of hydrolysis, $k_{2\text{-ODNB}}/k_{3\text{-ODNB}}$, was found to be about 29.[2]



The observed preference for endo tricyclic product **2** is surprising since examinations of molecular models indicate that steric control of attack at C-3 in **4** will favor exo approach. Furthermore, modified Westheimer calculations[3] of the atomic coordinates and torsional angles of planar **4** (with tricyclo[3.3.0.0^{2,8}]octan-3-one as a model) show that the endo lobe of the empty p_z orbital at C-3 is oriented for maximum overlap *only* with the C-2–C-8 bent cyclopropyl bond again suggesting that exo nucleophilic attack should predominate.

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[3] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wirtz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971); N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972). We are indebted to Professor Allinger for calculations on this structure and for stimulating discussions.