of I with the oxygen atom donor molecule (Scheme I, IVa) or as an [$Fe^{2+}O \leftrightarrow Fe^{4+}{=}O$] intermediate (Scheme I, IVb). Finally, the observation that neither II nor III is capable of catalytic oxygen atom transfer chemistry precludes their direct active involvement in the proposed scheme.

The data presented above is consistent with two possible mechanisms for oxygen atom transfer: (i) coordination of iodine of PhIO to the Fe^{2+} center resulting in oxygen activation[27] (IVa) or (ii) an oxygen rebound process whereby the oxygen atom from PhIO is transferred to substrate via the formation of an Fe–oxenoid species[7d] (IVb). Although the details of the reaction are under investigation, we prefer mechanism ii on the basis of the qualitative similarity of chromophore IV produced by either PhIO, C_6F_5IO, or excess peracid (*m*CPBA, PPAA), the observed reactivity of I with peracids, the quantitative conversion in the absence of substrate of I to III (via IV), the similarity of the observed product distribution with that generated by FeTPP-Cl and PhIO[7d], and the production of methyl phenyl sulfoxide and sulfone from methyl phenyl sulfide and sulfoxide, respectively. Since sulfide to sulfoxide and sulfoxide to sulfone transformations are catalyzed by metal–oxo species, the oxidation of cyclohexene must also involve such a species.[28] Furthermore, the observation that II is unable to act as an oxygen atom transfer catalyst in the presence of PhIO is inconsistent with a simple PhIO adduct of I or II acting as the active species. Work directed toward elucidating the mechanism of oxygen atom transfer reactions by I, determination of the nature of the active catalyst, the kinetic/structural characterization of species IV, and understanding the relevance of these observations to non-heme Fe containing monooxygenases is in progress.

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Spectroscopic Observation of Individual sp^3-Nitrogen Stereoisomers. Supersonic Jet Studies of 2-Aminobenzyl Alcohol‡

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Assessment of the stereodynamics at the template associated with a pyramidal trivalent nitrogen is complicated by the presence of two low-energy processes, nitrogen inversion and internal rotation about various single bonds.[1-6] Supersonic molecular jet laser spectroscopy has a number of particular advantages for conformational analysis for systems having low-energy interconversion processes:[7-9] the expansion results in molecules at near 0 K; the molecules are isolated; one 0_0^0 (origin) transition is observed for each individual stable conformation; and the resolution of the experiment is excellent (<1 cm^{-1}). Minimum energy conformations of a variety of alkyl-substituted and heterosub-

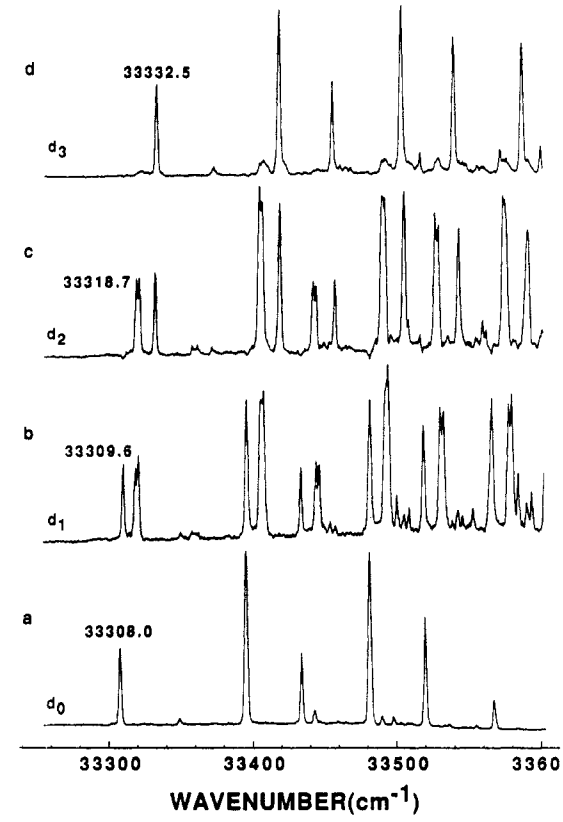

Figure 1. Mass-resolved excitation spectra of (a) 2-aminobenzyl alcohol (**2**), (b) 2-aminobenzyl alcohol-d_1 (**4a–4c**), (c) 2-aminobenzyl alcohol-d_2 (**5a–5c**), and 2-aminobenzyl alcohol-d_3 (**3**) about the 0_0^0 transition region.

‡Dedicated to Professor Tetsuo Nozoe, to commemorate his Beiju (88th birthday) and to honor his commitments to science.

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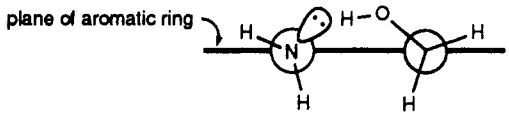
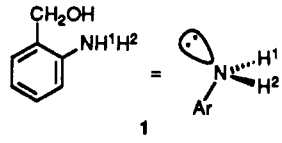
Chart I

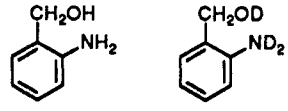


stituted aromatic compounds have been observed and their conformations determined by laser spectroscopy.[7-9] We herein report the first observation of spectra of individual isotopomers of a monosubstituted amine $ArNH^1H^2$, **1**, in which H^1 and H^2 represent diastereotopic hydrogen atoms under slow exchange conditions.[10]



1

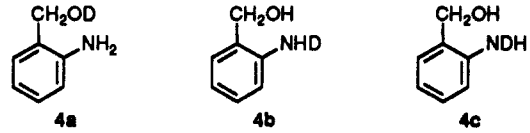
When compared to its all-protiated parent, a deuteriated analogue's first 0_0^0 transition will typically shift to the blue (to higher energy) while all vibronic transitions will shift to the red (to lower energy) relative to that origin.[8d] These isotope effects allow one to distinguish between origin and vibronic transitions.[8d] The mass-resolved excitation spectra[11] of 2-aminobenzyl alcohol (**2**) and its trideuteriated derivative **3** are shown in Figure 1a and



2 **3**

1d, respectively. Comparison of parts a and d of Figure 1 demonstrates that only a single origin transition is present in each spectrum, since each of the five transitions to the blue of the 0_0^0 transition in Figure 1d has a small but definite red shift relative to those in Figure 1a. In addition, the size of these isotope shifts (ca. 3-5%) demonstrates that the observed progressions are not due to motion involving either the NH_2 group or the OH group, but rather due to motion of the entire CH_2OH group in the excited electronic state.

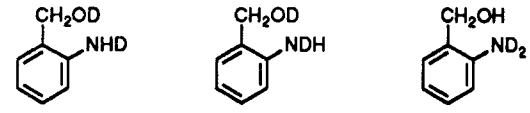
We now distinguish between 2-aminobenzyl alcohol species in which the amino hydrogen atoms H^1 and H^2 are nonequivalent.[10] The $S_1 \leftarrow S_0$ spectrum observed in mass channel m/z 124 (corresponding to 2-aminobenzyl alcohol-d_1 **4** is shown in Figure 1b.



4a **4b** **4c**

The spectrum of **4** is readily interpretable based on the spectra of **2** and **3**: each single transition of **2** and **3** has become a "triplet" in the spectrum of **4**. Each triplet can be further resolved into a single feature and a doublet to higher energy (cm^{-1}) (resolved by ca. 1 cm^{-1}). We interpret these three peaks as arising from the superposition of three spectra, one each for **4a-4c**. The lowest energy feature of the triplet is suggested to arise from **4a**, while the doublet feature is suggested to be associated with structures **4b** and **4c**, in which the two amino hydrogen atoms are diastereotopic.[10] Based on the perpendicular conformation of benzyl alcohol,[7] and on the expected intramolecular hydrogen bonding in **2** in the expansion gas, Chart I illustrates one possible geometry for 2-aminobenzyl alcohol.[10]

The mass-resolved excitation spectrum observed when monitoring mass channel m/z 125 for 2-aminobenzyl alcohol-d_2 (**5**)



5a **5b** **5c**

is shown in Figure 1c. This spectrum is remarkably similar to the spectrum of **4** (Figure 1b), with the exception that the relative positions of the singlet and the doublet are interchanged. Based on the above considerations, Figure 1c arises from the superposition of features from the spectra of **5a-5c**.

The individual diastereomers[10] of **4** and **5** are thus each stable over the time scale of the experiment and can be observed uniquely. The spectra of **4a-4c** and **5a-5c** are consistent with the number of isomers for each compound and the observation that deuterium substitution on the nitrogen atom produces a larger $S_1 \leftarrow S_0$ isotope shift than deuterium substitution on the oxygen atom. The switch in singlet-doublet positions going from Figure 1b to Figure 1c is also consistent with the location of the deuterium atoms in **4a-4c** compared to **5a-5c**: the lower 0_0^0 transitions obtain for the species having a CH_2OD moiety. Upon optical excitation ($S_1 \leftarrow S_0$), the force constants for the amino moiety must change more than those of the hydroxyl moiety.

To our knowledge, this work represents a unique experimental observation of spectra of the individual isotopomers of a monosubstituted amine. Future publications will disclose recent results on chemical reactions in intramolecularly hydrogen bonded systems observed by using these laser jet techniques.

(10) Under conditions in which rotation about $\tau(C_2-C_1-C_\alpha-O)$ is frozen and $\tau \neq 0°$ or $\tau \neq 180°$, H^1 and H^2 are diastereotopic.

(11) The experiment is performed as follows. A sample is irradiated with a laser of energy ν_1, resulting in the generation of the first excited singlet state ($S_0 \rightarrow S_1$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($S_1 \rightarrow I^+$). The ions are detected in given mass channels by time of flight mass spectroscopy, such that only ion current representing a chosen m/z is recorded. The energy of the ν_1 laser is changed, and absorption spectra of mass-selected species are obtained.

Phospholipase A_2 Engineering. 4. Can the Active-Site Aspartate-99 Function Alone?[1]

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The Asp···His···Ser "catalytic triad" is the key catalytic vehicle for serine proteases.[3] Recently this class of enzymes has been extended to include lipases.[4] While the catalytic roles of His and Ser have been relatively well established,[3] that of Asp has been a subject of debate. At least three possible roles have been suggested for the Asp: (a) orienting the conformation of His;[5] (b) stabilizing the appropriate tautomer of His;[5] and (c) neutralizing the positive charge of His during the reaction.[6] Strong evidence for role b has been provided in a recent study which

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