Stable Conformations of Benzylamine and N,N-Dimethylbenzylamine

S. Li, E. R. Bernstein,* and J. I. Seeman

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 (Received: June 1, 1992)

Mass-resolved excitation spectra (MRES) of deuterated and nondeuterated benzylamine, N,N-dimethylbenzylamine, and a number of their 4-ethyl-, 3-methyl-, and 3-fluoro-substituted derivatives are studied. The equilibrium conformations of these compounds are determined. In particular, the general torsion angle \( \tau_1 \) \( \left( C_{ortho} - C_{para} - C_{ortho} - N \right) \) is verified as near 90° and the angle \( \tau_2 \) is determined for both benzylamine \( \left( \tau_2 = (C_{para} - C_{ortho} - N - H) \right) \) and N,N-dimethylbenzylamine \( \left( \tau_2 = (C_{para} - C_{ortho} - N - C) \right) \). Torsional vibration progressions associated with the amino group in the first excited singlet state are identified and discussed. Both molecules are suggested to be nonrigid with respect to the \( \tau_1 \) and \( \tau_2 \) coordinates.

Introduction

Through the application of supersonic jet cooling techniques and mass-resolved excitation spectroscopy, we have been able to resolve the minimum-energy geometries of a number of substituted aromatic hydrocarbons and N-heterocycles. These systems include various \( \text{C}_n \) through \( \text{C}_8 \) alkyl-substituted benzenes, \(^3\) styrenes, \(^4\) allylbenzene, \(^5\) \( \text{C}_8 \) through \( \text{C}_3 \) alkyl-substituted pyrazines and pyridines, \(^6\) benzyl alcohol, \(^6\) methoxy- and ethoxybenzenes, \(^7\) phenethyl alcohol, \(^8\) and benzyl methyl ether. \(^9\) The stable geometry (minimum-energy conformations) for the general \( C_{ortho} - C_{para} - C_{para} - X_2 \) (where \( X \equiv \text{C} \) or \( \text{O} \), single bonded) torsion angle \( \tau_1 \) is found to be ca. 90° based on both experimental studies and semiempirical quantum mechanical calculations.\(^1\)\(^2\)

Previous calculational studies of benzylamines (BA) (Scheme I) suggest that the \( C_{ortho} - C_{para} - C_{ortho} - N \) torsional angle \( \left( \tau_1 \right) \) is approximately 90°.\(^10\) We have recently reported\(^1\) that benzylamine does indeed have this conformation. In this paper, we elaborate on this recent Letter and present a full report of our experimental and theoretical studies of the conformations of substituted benzylamines and \( N,N \)-dimethylbenzylamines. On the basis of these studies, we determine the equilibrium conformations of benzylamine and \( N,N \)-dimethylbenzylamine. In particular, benzylamine is found to have both perpendicular \( \left( \tau_1 \approx 90° \right) \) anti \( \left( \tau_2 \approx 60° \right) \) and gauche \( \left( \tau_2 \approx 180° \right) \) conformers under our experimental conditions, with the anti conformer of lower energy (higher concentration), and \( N,N \)-dimethylbenzylamine is found to have only a perpendicular gauche \( \left( \tau_1 \approx 90°, \tau_2 \approx 180° \right) \) conformation. Additionally, torsional vibration progressions are identified in the \( S_1 \) electronic state for a number of the benzylamines studied.

Experimental Procedures

Spectroscopy. Mass-resolved excitation spectra (MRES) reported in this work are all obtained with two photons \( (1 \leftrightarrow S_1 \leftrightarrow S_0) \) generated from a single Nd:YAG pumped dye laser.\(^1\) The output of the dye laser (LDS-698 or LDS-750) is doubled and mixed (with 1.064-\( \mu \)m Nd:YAG fundamental) in order to excite and ionize the various molecules studied. Molecules are cooled as previously described.\(^1\)

Samples. Benzylamine (BA), \( N,N \)-dimethylbenzylamine (DMBA), 3-fluorobenzylamine (3FBA), and 3-methylbenzylamine (3MBA) are purchased from Aldrich Chemical Inc. Other compounds, 4-ethylbenzylamine (4EBA), 3-methyl-\( N,N \)-dimethylbenzylamine (3MDMBA), 3-fluoro-\( N,N \)-dimethylbenzylamine (3FDMBA), and 4-ethyl-\( N,N \)-dimethylbenzylamine (4EDMBA), and all the deuterated compounds discussed are synthesized as will be reported in a subsequent publication.\(^1\) All the samples are used as provided without additional purification.

Calculations. Two algorithms are employed to calculate structures, conformational energies, and atomic partial charges for the various benzylamines investigated: MOPAC 6.1\(^3\) routines with a PM3 Hamiltonian augmented and improved for heteroatoms (e.g., N, O, etc.) and Gaussian 88 (ab initio restricted Hartree–Fock) routines.\(^14\) For the latter approach STO-3G and 3-21G* basis sets are used for various systems as indicated below.
Stable Conformations of Benzylamine and Derivatives

Results

Spectroscopy of Benzylamines. The mass-resolved excitation spectrum of benzylamine for the $S_1 \rightarrow S_0$ origin transition region ($0 \leq 250 \text{ cm}^{-1}$) is displayed in Figure 1a. The spectrum appears to contain a single origin (see below, however) at 37410 cm$^{-1}$; this pattern is repeated for the 6a$_2$ transition at 38049 cm$^{-1}$. At this level of resolution, the spectrum of BA is consistent with a single minimum-energy BA conformation existing in the supersonic expansion. The weak features at approximately 45, 80, 165, etc. are believed to be components of a progression in the low-energy torsion mode associated with motion in the $\tau_1$ coordinate. The feature at 104 cm$^{-1}$ is most likely a low-energy ring mode.

Assuming (for the moment) a single conformation for BA under these experimental conditions, the geometry of this conformation can be ascertained through the study of 4-ethyl-, 3-methyl-, and 3-fluorobenzylamines. The method takes advantage of "structural logic" which reduces finally to "simple counting" of identified origin transitions. For example, if the C$_2$-N bond in benzylamine is perpendicular to the plane of the aromatic ring [\( \tau_1 = \tau(C_{noo} - C_{no} - C - N) \approx 90^\circ \)] or is simply just out of the plane of the ring [\( \tau_1 \gg 0 \)], 4-ethylbenzylamine will display two origin transitions: one for the syn (both ethyl and amino groups are on the same side of the ring) and anti (ethyl and amino groups are at different sides of the ring) conformers. Recall that the C$_2$-C$_a$ bond of the ethyl group is known to be perpendicular to the aromatic plane of ethylbenzene and that it is known not to change conformation with 3/4-alkyl substitution. Deuteration of the various substituent groups can be further employed in many instances to assist in the location of origin transitions. If the angle $\tau_1 = 90^\circ$ in BA, the spectrum of 4-ethylbenzylamine would contain only one origin transition. On the other hand, $\tau_1 \approx 90^\circ$ yields one conformer for 3-methylbenzylamine and $\tau_1 = 0^\circ$ yields two conformers for 3-methylbenzylamine. If $\tau_1$ is between $0^\circ$ and $90^\circ$, or $\tau_2 = \tau(C_{noo} - C_{no} - N - H)$ is approximately $180^\circ$, one may also expect two conformers for 3-substituted benzylamines.

Nevertheless, the origins of these latter two conformers may not be resolved spectroscopically under current available resolution if $\tau_1$ is close to $90^\circ$ or perhaps for any value of $\tau_2$. Note that the size of the syn/anti $S_1 \rightarrow S_0$ transition energy difference for 4-ethyl-substituted aromatics (e.g., 4-diethylbenzene, 4-ethylbenzyl alcohol, and others$^{12,44}$) is typically ca. 5 cm$^{-1}$. In using these techniques for the benzylamine systems, one can anticipate $S_1 \rightarrow S_0$ splitting for the two conformers of similar size.

Consistent with the above-outlined procedure, we have obtained spectra of 3-methylbenzylamine (and some of its deuterated analogues) and 4-ethylbenzylamine (and some of its deuterated analogues), as displayed in Figure 1b-f. Figure 1b,c displays spectra of 3-methylbenzylamine and 3-methylbenzylamine-$\omega$-$\omega$-$d_2$. The origin doublet, in this instance, is known to be due to the $a \leftrightarrow a$ and $e \leftrightarrow e$ internal free rotor state transitions associated with the ring-substituted methyl group at 3$^\circ$. Since no additional origin splittings can be identified for these molecules, the spectra presented demonstrate that the angle $\tau_1$ is close to $90^\circ$ for benzylamine. Figure 1d-f presents spectra of the various 4-ethylbenzylamines ($d_0$, $\alpha$-$\alpha$-$d_2$, and $\omega$-$\omega$-$d_2$). These spectra are consistent with the others of Figure 1 and show two origins (conformers). Thus $\tau_1$ is not equal to $0^\circ$ and is ca. $90^\circ$.

Figure 2 displays the spectrum of 3-fluorobenzylamine. One origin at 37393 cm$^{-1}$ is quite easy to identify from its intensity and the ca. 110 cm$^{-1}$ progression built on it. This feature is not the first one in the spectrum, however. The two initial transitions in this spectrum (at 37292 and 37320 cm$^{-1}$) are not hot bands (based on expansion pressure/cooling experiments) and can be tentatively identified as origins. The feature at 37320 cm$^{-1}$ has a 50 cm$^{-1}$ progression built on it.

These spectra suggest that two conformers are present for benzylamine: one with $\tau_1 \approx 90^\circ$ and $\tau_2 \approx 60^\circ$ (anti) and another with $\tau_1 \approx 90^\circ$ and $\tau_2 \approx 180^\circ$ (gauge). $\tau_1$ could be different from $90^\circ$ for the gauche conformer as long as this difference does not generate an origin splitting in 3-substituted benzylamines. The identification of two conformers for benzylamine would imply that our initial assignment of the benzylamine spectrum is incorrect: a more careful examination of the benzylamine spectrum would thus be required.

Figure 3 presents such a study of various amine deuterated benzylamine-$d_0$, -$d_1$, and -$d_2$ $0^\circ$ transitions. Note the following
MRES of Benzylamine

Figure 3. Higher dispersion scan of the benzylamine-$d_0$, $d_1$, and $d_2$ spectra. The conformers in (b) are drawn in Newman projection viewed along the N-C bond. Conformer assignments are made according to the $d_i$ spectrum.

Observations for the spectra presented in Figure 3: (1) the $^{13}$C isotope effect shifts the spectrum about 3 cm$^{-1}$ to the blue, (2) the $d_1$ spectrum consists of two features, one of roughly 10% the intensity of the other, (3) a comparison between the $d_0$ and $d_2$ spectra suggests that the structure of the origin is not due to unresolved rotational envelope structure, (4) the $d_0$ and $d_2$ spectra suggest that the smaller intensity component of the $d_3$ spectrum is red-shifted with respect to its counterpart in the $d_0$ spectrum, and (5) the $d_1$ spectrum is intermediate between the $d_0$ and $d_2$ spectra with respect to both red shift and intensity. These observations are consistent with a lower energy anti conformer and a higher energy gauche conformer of benzylamine existing simultaneously in the supersonic expansion. These assignments are presented in the figure. The size of the energy separation for the $S_1$ -- $S_0$ transitions of the two conformers is small, consistent with expectations for an anti/gauche $\tau_2$ orientational difference between the two conformers.

To demonstrate that this assignment is at least reasonable, the spectra of ethylbenzene-$\beta$-$d_0$, $d_1$, and $d_2$ are presented in Figure 4.

MRES of Ethylbenzene

Figure 4. Ethylbenzene-$\beta$-$d_0$, $d_1$, and $d_2$ spectra. See Figure 3 for description. Obtained for comparison with benzylamine-$d_0$, $d_1$, and $d_2$ spectra.

Figure 5. MOPAC 6 structures for benzylamine. The anti conformer is lower in energy.

TABLE I: Calculated Conformation Energies and Angles for Benzylamine

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<th>Method</th>
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<th>$\tau_2$</th>
<th>Energy</th>
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<td>3-21G*</td>
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<td>A. Anti</td>
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<td>B. Gauche</td>
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<td>3-21G*</td>
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*The angles (in degrees) are defined in Scheme I, and the energies (in hartrees) are given as the total energy (electronic energy and core-core repulsion) for the PM3 calculation and the ground-state potential energy ($E(R)$) for the Gaussian 88 basis set calculations. See Scheme I.

Clearly, the different possible orientations of the terminal deuterium can be discerned, and the relative intensities of the features are consistent with the known geometry of ethylbenzene. We consider this strong support for the benzylamine anti/gauche assignment based on both relative intensities and the size of the conformer energy difference.

Calculations on Benzylamine. The results of both MOPAC 6 and Gaussian 88 calculations are summarized in Table I. Geometries calculated from MOPAC 6 are also displayed in Figure 5. Both the STO-3G and the 3-21G* basis sets calculate a planar ($\tau_1 = 0^\circ$) geometry of comparable energy (ca. 500 cm$^{-1}$) to the
perpendicular anti and gauche conformers reported above. In general, the calculations show that two or three conformers of comparable energy are possible for benzylamine. The energy separation between these conformers is of the order of a few hundred cm$^{-1}$, which conformer is calculated to be lowest in energy depends on both calculational algorithm and basis set chosen. The torsion angle $\tau_1$ in the gauche conformer also varies greatly from basis set to basis set. A plot of potential energy vs $\tau_1$ based on a MOPAC 6 calculation shows only very small (50 cm$^{-1}$) energy change with a 30° angle change in $\tau_1$ (see Figure 6). Thus, $\tau_1 \approx 90^\circ$ for this form implies a large variation in angle for a small change in energy. Note also that, for a ca. 100-cm$^{-1}$ torsional mode in $\tau_1$, the zero-point energy in the $\tau_1$ coordinate would delocalize the structure between 60° and 120°. In this regard, and most likely with respect to $\tau_2$ motion as well, benzylamine is a nonrigid molecule with very large amplitude vibrational motion in both displacements.

**Spectroscopy of $N,N$-Dimethylbenzylamines.** The mass-resolved excitation spectrum of $N,N$-dimethylbenzylamine (DMBA) is presented in Figure 7a. The single origin in this spectrum falls at 37 511.5 cm$^{-1}$. Comparison of this spectrum with that of the DMBA-d$_8$ spectrum of Figure 7b suggests that only a single origin is present in both spectra based on the large progression intensity differences observed. The DMBA-d$_8$ origin falls at 37 540 cm$^{-1}$. The possible origin assignments for features at $0_{0}^\pm + 40$ (37) cm$^{-1}$ and $0_{1}^\pm + 106$ (97) cm$^{-1}$ in the DMBA (-d$_8$) spectra will be further discussed below. These features can be assigned as members of a low-frequency dimethylamino group mode progression. Thus, the spectrum of DMBA shows only a single origin feature, consistent with a single conformation present in the low-temperature sample.

This suggestion is confirmed by the spectra of 4-ethyl-$N,N$-dimethylbenzylamine (4-EDMBA) and its ethyl-d$_5$-dimethylamino-d$_8$ analogue (4-EDMBA-d$_1$-d$_8$). These spectra (Figure 7c,d) clearly indicate a doublet origin for the syn/anti conformations of the two substituent side chains. Through analogy with the spectra of other 4-ethyl-substituted aromatics, we conclude that the dimethylamino group is out of the plane of the ring.

Figure 8 contains the spectra of 3-methyl- and 3-fluoro-substituted DMBA and their various deuterium-substituted species. All spectra consistently point to two conformers of these species. (a) $0_{0}^\pm S_2 \leftarrow S_0$ region of 3-methylbenzylamine; (b) $0_{0}^\pm S_1 \leftarrow S_0$ region of 3-methyl-$N,N$-dimethylbenzylamine-$a,a,d_2$; (c) $0_{0}^\pm S_1 \leftarrow S_0$ region of 3-methyl-$d_1,d_8$-dimethylbenzylamine-$a,a,d_2$; (d) $0_{0}^\pm S_2 \leftarrow S_0$ region of 3-methyl-$d_1$-dimethylbenzylamine-$a,a,d_2$; (e) $0_{0}^\pm S_1 \leftarrow S_0$ region of 3-fluorodimethylbenzylamine; (f) $0_{0}^\pm S_2 \leftarrow S_0$ region of 3-fluorodimethylbenzylamine-$d_4$.

The 3-methyl- and 3-fluoro-substituted DMBA show two origins in the spectra presented in Figure 8. The 3-methyl spectra of Figure 8a–d evidence two clear origins as the main initial doublet.
**TABLE II: Calculated Conformation Energies and Angles for N,N-Dimethylbenzylamine**

<table>
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<th>( \tau_1 )</th>
<th>( \tau_2 )</th>
<th>Energy</th>
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<td>65.2</td>
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<td>STO-3G</td>
<td>89.8</td>
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<td>PM3</td>
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<td>-52.52911</td>
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*The angles (in degrees) are defined in Scheme I, and the energies (in hartrees) are given as the total energy (electronic energy and core-core repulsion) for the PM3 calculation and the ground-state potential energy \( E(R) \) for the Gaussian 88 basis set calculations. See Scheme I.

**SCHEME II**

This doublet is further split by the 3-methyl group as is demonstrated by the 3-methyl-d4 spectrum of Figure 8e. Some portion of the dimethylamine group must be oriented syn and anti with respect to the 3-methyl substituent. The origin splitting is small (ca. 7 cm\(^{-1}\)), and this is consistent with a \( \tau_2 \) orientational effect rather than a \( \tau_1 \) (0° vs 90°) orientation effect. The feature at 35 cm\(^{-1}\) in these spectra can be eliminated as a possible additional origin by comparison with the spectra of 3-fluoro-N,N-dimethylbenzylamines shown in Figure 8c. Only two origins are present in each of these latter spectra. Two harmonic vibrational progressions with \( \Delta \nu = 29 \) and 37 cm\(^{-1}\) are found built on the origins at 37,336 and 37,361 cm\(^{-1}\) of 3FDMA, respectively. The rest of the transitions in the origin region are of negligible intensity: the possibility of an additional origin for DMBA can therefore be eliminated. Thus, some part of the dimethylamine group is asymmetrically nonplanar and some part of this group is asymmetric with respect to the 3-position on the ring.

**Calculations on N,N-Dimethylbenzylamine.** The MOPAC 6 and Gaussian 88 calculated energies and conformations for N,N-dimethylbenzylamine are presented in Table II. Both calculational techniques yield anti and gauche conformers as characterized in Scheme II. The MOPAC 6 calculation yields an additional planar form included in Table II.

The general, although not consistent, results of these calculations are that two or three conformers exist of this molecule. The planar conformer (Scheme II) is only found by the semianalytical calculation. The Hartree–Fock calculation yields the gauche conformer lower in energy than the anti conformer by roughly 450 cm\(^{-1}\). The lack of consistency in these results precludes all but the most general conclusions based on the calculations: the experimental findings, \( \tau_1 \sim 90° \) and \( \tau_2 \sim 180° \), are not contradicted by the calculation. The potential surface for \( \tau_1 \) motion is expected to be very shallow with only a weak restoring force. The zero-point motion of this coordinate would greatly delocalize the structure in \( \tau_1 \). Similar behavior can be suggested for the \( \tau_2 \) coordinate as well. Again, this molecule must be viewed as nonrigid in the \( \tau_1 \) and \( \tau_2 \) coordinates with very large amplitude vibrational motion in both displacements.

**Discussion**

**Benzyliamine Geometry.** Benzyliamine has two conformations in our experiments: in both instances \( \tau_1 \sim 90° \) while \( \tau_2 \sim 60° \) (anti) or \( \sim 180° \) (gauche). The anti conformer is clearly the lower energy conformer of the two based on the relative intensity of the anti/gauche origin features presented in Figure 3.

Calculations are not very helpful in deciding the equilibrium geometries of this molecule because they do not present a clear basis set or algorithm-independent set of results. Apparently, the nitrogen atom in benzyliamine makes the calculations much less reliable than the comparable calculations for the ethylbenzened because the potential surface for these coordinates is so shallow and the restoring force is so small. The zero-point motion in these coordinates is very large.

**N,N-Dimethylbenzylamine Geometry.** The situation is similar for the dimethylbenzylamine, \( \tau_1 \sim 90° \) and \( \tau_2 \sim 180° \), and the calculations generate three possible low-energy structures within a few hundred cm\(^{-1}\) of one another. Again, the calculations are not a reliable predictor of the minimum-energy conformation of this molecule. The zero-point motion for these coordinates probably exceeds 50°.

**Vibrational Progressions.** Due to the nonrigid nature of these molecules and the low-energy displacements of the two angle bending modes involving torsion (\( \tau_1 \) and \( \tau_2 \)) and \( \tau(C_{\text{NCH}}-C_{\text{CH}_2}-N) \) (wag), any one of these vibrations might be expected to appear as a progression in the \( S_i \leftrightarrow S_{i+1} \) spectra. Additionally, calculations suggest that motion in either the \( \tau_1 \) or \( \tau_2 \) coordinate has only a small restoring force, a shallow potential surface, and a small force constant. Since motion in \( \tau_1 \) appears to be the lowest energy mode, one can expect that this displacement would be the main progression forming mode in \( S_1 \leftrightarrow S_2 \) spectra.

Such a mode shows up in all spectra observed: in BA the mode is \( \sim 50 \) cm\(^{-1}\), in 3-MBA and 3MBA-o-d4 the mode is 55 and 74 cm\(^{-1}\), respectively; in 4EBA and 4EBA-o-d4, the mode is \( \sim 65 \) cm\(^{-1}\) in 3FBA, gauche and anti, the mode is 50 and 100 cm\(^{-1}\), respectively; and in DMB, the mode is close to 70 cm\(^{-1}\) somewhat less clearly resolved than in the other instances. Positive identification of these features with one particular coordinate is not obvious through this series because the mode clearly involves more than one isolated symmetry coordinated as can be seen from its increase in energy upon deuteration of the 3-substituted benzyliamines. Initially, one must identify the fundamental frequency of the observed mode(s), as even this may not be certain throughout the series of molecules studied.

Only a complete normal-coordinate analysis of the low-energy modes of these species will reveal the true nature of the observed progressions and the parameter of the (mixed) modes involved. The modes appear to be fairly harmonic at least for the first few overtones so a harmonic analysis may be sufficient to understand the low-energy potential surface of these molecules.

**Conclusions**

Spectroscopic and theoretical studies for both benzyliamine and N,N-dimethylbenzylamine reach the following conclusions. (1) The \( C_{\text{NCH}}-N \) bond is close to perpendicular to the ring plane \( (\tau_1 \sim 90°) \) in both molecules. (2) The orientation of the N-H bonds in benzyliamine is symmetrically over the ring \( (\tau_2 \sim 60°) \) for the minimum-energy conformer. (3) A second somewhat higher energy conformer exists in low concentration for benzyliamine in which one hydrogen of the amino group is toward the ring and the other is away from the ring \( (\tau_2 \sim 180°) \). (4) N,N-Dimethylbenzylamine has a gauche geometry: \( \tau_1 \sim 90° \) and \( \tau_2 \sim 180° \). (5) In neither case are the calculations accurate enough to be of predictive value for the minimum-energy geometries of these two molecules. (6) Large-amplitude (±30–50°) zero-point displacements are expected for both \( \tau_1 \) and \( \tau_2 \) coordinates in these molecules, and one should consider both benzyliamine and N,N-dimethylbenzylamine nonrigid molecules with respect to these displacements.

**Acknowledgment.** This work was supported in part by grants from ONR and NSF.
Tapered Velocity Coupling Method for Optical Waveguide Raman Scattering Spectroscopy. Application to Iron(III) Phosphate Thin Films

Takanori Mitsuhata, Shuji Fujii, Koichi Itoh,*
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan
Kiminori Itoh, and Masayuki Murabayashi
Institute of Environmental Science and Technology, Yokohama National University, Tukiwada, Hodogaya-ku, Yokohama 240, Japan (Received: June 2, 1992; In Final Form: July 20, 1992)

The application of the tapered velocity coupling method was proposed to measure optical waveguide Raman (OWG-R) spectra of a thin film, which shows large attenuation due to absorption and/or scattering. The method was applied to record the spectra of an iron(III) phosphate thin film (ca. 0.2 μm) deposited on a K⁺-doped glass waveguide. The thin film was fabricated to have a tapered structure at both ends. One of the TE and TM modes of the 514.5-nm Ar⁺ laser line in the glass waveguide was adiabatically transferred to the thin film through the tapered structure, so that the optical field intensity becomes concentrated almost completely within the thin films. Theoretical calculations indicated that the adiabatically coupled TE-0 mode has its intensity maximum near the interface between the film and the K⁺-doped glass waveguide, while the TM-0 mode has its intensity maximum near the surface (or the interface between the film and air). The OWG-R spectra measured with the TE-0 and TM-0 modes give rise to a P-O stretching band near 1060 and 1030 cm⁻¹, respectively, suggesting differences in structure and/or composition between the interface and the surface. Raman spectra of iron phosphate treated at various temperatures (100–200 °C) indicated that a conversion from an amorphous to a crystalline state induced by the treatment causes the shift of the P-O stretching band from 1049 to 1030 cm⁻¹. Furthermore, the OWG-R results indicate a difference in crystallinity between the surface and interface regions of the iron phosphate thin film; i.e., the surface region exists in a crystalline state, while the interface assumes an amorphous state, giving the band at 1060 cm⁻¹. This conclusion was supported by X-ray diffraction measurements of iron phosphate thin films treated under various temperatures.

References and Notes

(2) Schrödinger, E. Z. Phys. 1926, 38, 95.
(3) Schrödinger, E. Z. Phys. 1926, 38, 98.
(9) Schrödinger, E. Z. Phys. 1926, 38, 104.

Introduction

The first optical waveguide Raman (OWG-R) spectral measurement was performed on polymer films of about 1-μm thickness by Levy et al. Rabolt and Swalen have carried out a series of OWG-R spectral measurements on thin polymer films and monolayers and placed this technique on a firm basis. Observation of Raman scattering with guided modes of transverse electric (TE) and transverse magnetic (TM) waves in an asymmetric slab waveguide can give a spectrum with sufficient signal-to-noise ratio of the slab itself. This is mainly due to high optical field intensity of the guided mode confined within the slab and due to an increased scattering volume. Besides being very efficient for observing Raman spectra of very thin films, OWG-R spectroscopy provides information about depth profiles of structures and composition of the films. Especially in the case of an OWG with a laminated structure (or a composite OWG consisting of at least two layers), depending on both the thicknesses of the layers and their relative refractive indices, the optical field intensity of a guided mode can become concentrated mainly either in one of the layers or in an interfacial part of the OWG. Thus, from the OWG-R spectra measured with the waveguide mode we can get information about structures of a specific part of the waveguide (a particular layer or an interface). This has been well established by the OWG-R studies on laminated polymer samples. The amplitude of scattering is proportional to the square of the surface roughness, so that thin film OWGs often show large attenuation. For instance, theoretical calculations indicate that an OWG with the thickness of 0.1 μm and mean-square roughness of 2 nm gives attenuation of >100 dB/cm. In the case of such a thin film and the case where an optical waveguide material itself shows large attenuation due to absorption, it is difficult to measure the OWG-R spectra by usual techniques, because of a short optical waveguide streak (e.g., less than 10 mm). To overcome this disadvantage in the present paper, we propose application of the tapered velocity coupling method to OWG-R spectroscopy. In this method a miniband thin-film light-absorbing optical waveguide (with thickness of several tenth of micrometers and width of several millimeters, which is short enough to observe out-coupled light intensity) is deposited on a K⁺-doped glass OWG (with thickness of several micrometers). The former OWG has a tapered structure at both ends. Coupling of a laser beam to the composite OWG is accomplished at a part of the glass OWG (it was performed...