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Spectroscopic and Computational Studies of the Intramolecular Hydrogen Bonding of 2-Indanol

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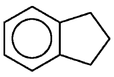
2-Indanol in its most stable form is stabilized by internal hydrogen bonding, which exists between the hydroxyl hydrogen atom and the π-cloud of the benzene ring. A comprehensive ab initio calculation using the MP2/cc-pVTZ level of theory showed that 2-indanol can exist in four possible conformations, which can interchange through the ring-puckering vibration and the internal rotation of the OH group on the five-membered ring. A potential energy surface in terms of these two vibrational coordinates was calculated. Density functional theory calculations were used to predict the vibrational frequencies and to help in normal mode assignments. Fluorescence excitation spectra of 2-indanol confirm the presence of the four conformers in the electronic ground and excited states. The spectral intensities indicate that, at 90 °C, 82% of the molecules exist in its most stable form with the intramolecular hydrogen bonding. The other isomers are present at approximately 11, 5, and 3%. The MP2/6-311++G(d,p) calculation predicts a distribution of 70, 13, 9, and 8% at 90°C, the experimental sample temperature.

Introduction

Over the past several years, we have been utilizing spectroscopic methods to investigate the structures, conformations, and potential energy surfaces (PESs)[1] of indan (IND)[2] along with the related molecules phthalan (PHT),[3−5] coumaran (COU),[6,7] and 1,3-benzodioxole (13BZD).[8,9] We have used laser-induced fluorescence (LIF) spectra of the jet-cooled molecules and ultraviolet absorption spectroscopy along with infrared and Raman spectroscopy and theoretical calculations (ab initio, DFT) to investigate the PESs of these molecules in their ground (S_0) and first excited $S_1(\pi,\pi^*)$ electronic states.[10] The structural and conformational changes in these two states have provided considerable insight into understanding the intramolecular forces and bonding of these molecules.



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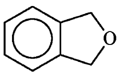

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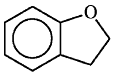

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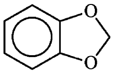

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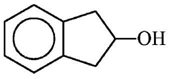

IND-ol

In the present paper, we turn our attention to 2-indanol (IND-ol), which is of special interest due to its possibility of intramolecular hydrogen bonding between the OH group and the benzene ring. The Chakrabouty laboratory in 2003 reported[11] a combined spectroscopic (two-photon ionization and dispersed fluorescence) and quantum chemistry calculation study of this molecule. They observed three isomers experimentally and their ab initio calculations estimated a hydrogen bond energy of 6.5 kJ/mol (540 cm^{-1}) for the most stable isomer. In our present work we present the infrared and Raman spectra of the IND-ol ground state and also the LIF spectra of the $S_1(\pi,\pi^*)$ state. In addition, we present high level ab initio and DFT calculations for the molecule for a large number of values for the ring-puckering and −OH internal rotation coordinates. From this a theoretical two-dimensional surface was constructed and this was then related to the experimental data.

After the completion of our work we discovered the very recent study of He and Kong[12] who examined the REMPI and ZEKE spectra of this molecule. These workers identified three conformers and assigned some vibronic levels to two of these. They also carried out ab initio and DFT calculations in order to obtain theoretical one-dimensional potential energy functions for the ground and excited states. Where appropriate, their results will be compared to ours. Another recent study has been published by Ottaviani et al.[13] They reported the rotational spectra of 2-indanol and its O−D isotopomer using free jet millimeter-wave absorption spectroscopy. Only the main conformer possessing the intramolecular hydrogen bonding was observed.

Experimental Section

2-Indanol was obtained from Aldrich as a white powder with a stated purity of 99%. Its melting point is approximately 70 °C. The sample was further purified by vacuum transfer and white crystals were obtained. For the liquid Raman experiment the sample was placed into a 1 mm tube, was evacuated, and then sealed. A metal wire was wrapped around the sample tube to heat the solid to 100 °C and to melt the sample. A Jobin-Yvon U-1000 double monochromator equipped with a charged-coupled detector (CCD) and an Innova I-100 argon ion laser operating at 5145 Å with 0.5 W of power were used. The Raman spectra of the solid were recorded using 150 mw of laser power. The infrared spectrum of the solid was obtained by dissolving it in CCl_4 and depositing it on a KBr window. After evaporation, white crystals were formed on the salt window. The mid-infrared spectrum was recorded using a Biorad FTS-60 equipped with a globar source, KBr beam splitter, and a triglycerin sulfate detector. A total of 256 scans at 1.0 cm^{-1} were averaged.

Fluorescence excitation spectra (FES) were obtained with a spectral resolution of 1 cm^{-1} on the previously described jet-cooled fluorescence excitation instrumentation.[14−16] Excitation to the electronic excited state was accomplished using a tunable

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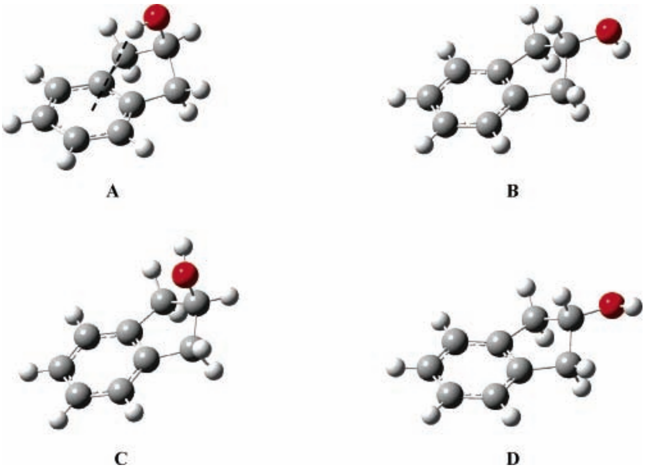


Figure 1. Four stable conformations of 2-indanol. The intramolecular hydrogen bonding present in the most stable conformer (structure A) is represented by a dotted line.

UV laser system which consists of a Continuum Powerlite 9020 Nd:YAG laser which pumps a Continuum Sunlite optical parametric oscillator (OPO). Visible output from the Sunlite OPO was frequency doubled using a Continuum FX-1 UV extension unit, which produced continuously tunable UV radiation from 355 to 225 nm with a resolution of 0.7 cm^{-1}. Helium and argon were used as backing gases with stated purities of 99.99%. Backing gas pressures were selected to obtain the optimal spectra and were typically at pressures between 1 and 20 atm.

Dispersed fluorescence (SVLF) spectra from the 0 ← 0 bands for the conformers were recorded on an ISA HR-640 monochromator equipped with a Spex Spectrum One CCD with a 2000 × 800 pixel chip. This CCD is UV antireflection coated and back-thinned, making it sensitive in the UV. The SVLF spectra were taken at ± 2 cm^{-1} resolution.

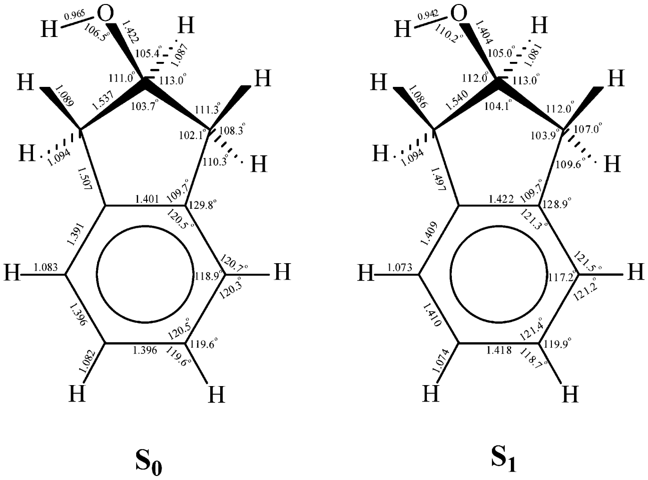


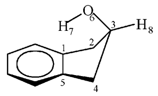
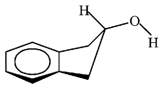
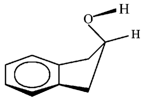
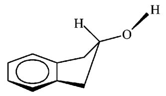
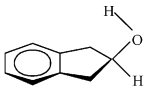
Figure 2. Calculated bond distances and angles of the most stable structure of 2-indanol for its S$_0$ and S$_1$ states calculated at the MP2/cc-pVTZ and CIS/6-311++G(d,p) levels of theory, respectively.

The electronic absorption spectra of the IND-ol vapor was also recorded using a Bomem DA8.02 Fourier transform spectrophotometer in the 20000−40000 cm^{-1} region. A deuterium lamp source, a quartz beam splitter, and a silicon detector were used. The vapor was contained in a 25 cm glass cell with quartz windows. Spectral acquisition was carried out at temperatures up to 250 °C. Beyond that temperature the sample starts decomposing. 15000 scans were recorded at 0.5 cm^{-1} resolution and averaged. However, since solid 2-indanol has a very low vapor pressure, only several weak UV bands, mostly in the 0 ← 0 region, were observed, and these were used to confirm some of the FES bands.

Computations

Ab initio calculations on the structure and vibrational frequencies of 2-indanol in the electronic ground and excited states have been previously reported.[11−13] The energies and structures of the lowest energy structures of the molecules in the S$_0$ electronic ground state were previously calculated using

TABLE 1: Calculated[a] Structural Parameters, Energies, Puckering Angles, OH Internal Rotation Angles, and Dipole Moments for the Conformations (A, B, C, and D) and Planar Structure (P) of 2-Indanol in Its Electronic Ground State

	 A	 B	 C	 D	 P
Bond distances (Å)					
$C_3–O_6$	1.422 (1.426)	1.413 (1.416)	1.424 (1.429)	1.417 (1.421)	1.423 (1.425)
$O_6–H_7$	0.965 (0.964)	0.963 (0.963)	0.962 (0.962)	0.962 (0.961)	0.963 (0.963)
$C_3–H_8$	1.087 (1.088)	1.091 (1.091)	1.093 (1.094)	1.096 (1.096)	1.087 (1.088)
Bond Angles (deg)					
$C_3O_6H_7$	106.5 (108.4)	107.2 (108.5)	107.6 (108.6)	107.8 (108.9)	107.0 (108.4)
$C_2C_3C_4$	103.7 (104.1)	103.8 (104.3)	104.4 (104.9)	104.1 (104.7)	106.6 (106.3)
$O_6C_3H_8$	105.4 (104.7)	105.2 (104.6)	110.4 (109.7)	110.7 (109.9)	104.0 (103.7)
Puckering Angle (deg)	35.4 (29.7)	-35.1 (-30.4)	31.1 (25.5)	-35.0 (-29.7)	0.0 (0.0)
Internal Rotation Angle (deg)	180.0 (180.0)	180.0 (180.0)	66.9 (63.0)	54.5 (52.3)	180.0 (180.0)
Total Energy (Hartrees)	-423.3316818 (-424.3550792)	-423.32948051 (-424.35422743)	-423.3296766 (-424.3537517)	-423.32954458 (-424.35415258)	-423.3257208 (-424.3520662)
Relative Energy (cm^{-1})	0.0 (0.0)	483.1 (186.9)	440.1 (291.3)	469.1 (203.4)	1308.3 (661.3)
Total Dipole Moments (Debye)	1.59 (1.39)	1.45 (1.36)	1.80 (1.47)	1.46 (1.36)	1.33 (1.25)

[a] MP2/cc-pVTZ theory was used. Results in parentheses are from the DFT-B3LYP/cc-pVTZ calculations.

TABLE 2: Comparison of Energies and Puckering and Internal Rotation Angles from Different Basis Sets

	MP2/cc-pVTZ				MP2/6-31+G(d,p)				DFT-B3LYP/cc-pVTZ			
	total energy (hartree)	relative energy (cm^{-1})	puckering angle (deg)	internal rotation angle (deg)	total energy (hartree)	relative energy (cm^{-1})	puckering angle (deg)	internal rotation angle (deg)	total energy (hartree)	relative energy (cm^{-1})	puckering angle (deg)	internal rotation angle (deg)
A	−423.33168184	0	35.4	180.0	−422.9342967	0	35.4	180.0	−424.35507920	0	29.7	180.0
B	−423.32948051	483	−35.1	180.0	−422.9317951	549	−35.1	180.0	−424.35422743	187	−30.4	180.0
C	−423.32967663	440	31.1	66.9	−422.9325933	374	31.5	69.5	−424.35375170	291	25.5	63.0
D	−423.32954458	469	−35.0	54.5	−422.9322436	451	−34.5	56.2	−424.35415258	203	−29.7	52.3
P	−423.32572080	1308	0.0	180.0	−422.9279627	1390	0.0	180.0	−424.35206620	661	0.0	180.0

the MP2/6-311++G(d,p) level of theory,[11] which is expected to give a good prediction of the geometry and the stability of the molecule. Density functional theory (DFT) has also been used to calculate the structure in the electronic ground state.[12,13] One-dimensional potential energy calculations of the S_0 state in terms of the ring puckering and internal rotation of the OH group in 2-indanol were obtained using MP2/6-31G(d,p)[11] and DFT-B3LYP/6-311++G(d,p)[13] computations. The calculations of the S_1 excited-state structures of 2-indanol and their relative stabilities were performed at the CIS/6-31+G(d) level of theory.[12]

In our present work we have carried out additional high level ab initio and DFT computations including the triple-ζ calculations. Figure 1 shows the four stable conformers which were studied. Conformer A with the intramolecular hydrogen bonding is the most stable. Figure 2 shows the calculated structures for conformer A for its S_0 and S_1 states. During the calculations it was observed that when the diffuse functions in the basis sets were not used, the relative energies of the other three conformers (B, C, and D) were rearranged as compared to the 6-311++G(d,p) basis set.[11] Nonetheless, conformer A with the intramolecular hydrogen bonding was the most stable in all cases.

In our work we have employed the cc-pVTZ basis set (triple-ζ) with the MP2 and DFT-B3LYP theories to predict the molecular structures and relative energies of the four minimum structures shown in Figure 1, and the planar structure as well, using the Gaussian 03 program.[17] The relative energies predicted by the MP2 with the triple-ζ basis set presented in Table 1 were found to be very similar to those predicted by the 6-311++G(d,p) basis set.[11] However, the effect of the triple-ζ basis set when used with the DFT-B3LYP theory (Table 1) gave more reliable predictions of the energies as well as the structures as compared to other basis sets.[12,13]

We have constructed an energy map to enhance our understanding of the intramolecular forces governing the structure

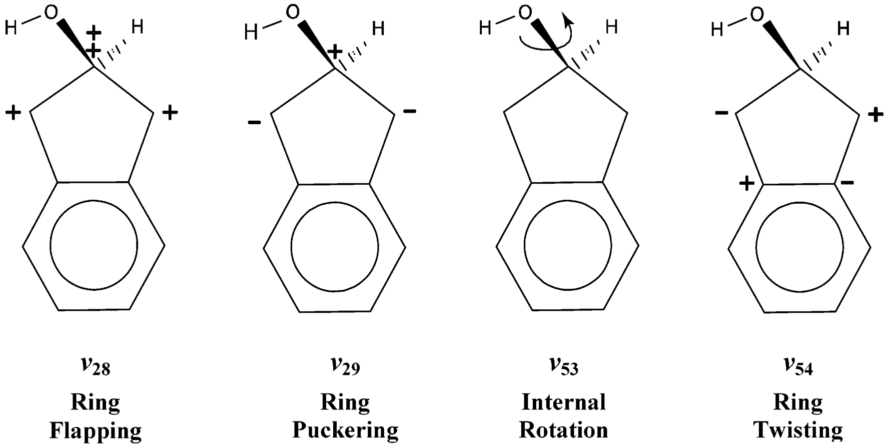


Figure 3. Four large-amplitude low-frequency vibrations of 2-indanol.

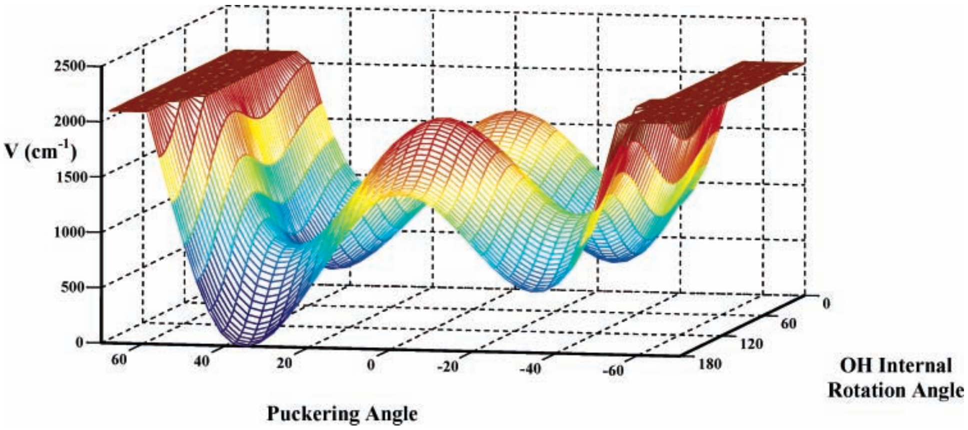


Figure 4. Calculated potential energy surface of 2-indanol in terms of its ring puckering angle (degrees) on OH internal rotation (degrees relative to 180° at the A conformation).

TABLE 3: Calculated Energies, Puckering Angles, and Internal Rotation Angles of the Transition Structures in the Energy Map of 2-Indanol

	MP2/cc-pVTZ				DFT-B3LYP/cc-pVTZ			
structure[a]	total energy (hartree)	relative energy (cm^{-1})	puckering angle (deg)	internal rotation angle (deg)	total energy (hartree)	relative energy (cm^{-1})	puckering angle (deg)	internal rotation angle (deg)
P	−423.32572080	1308	0.0	180.0	−424.35206620	661	0.0	180.0
S_{AB}	−423.32566750	1320	−2.5	180.0	−424.35203550	668	−2.5	180.0
S_{AC}	−423.32837524	726	33.1	116.1	−424.35223003	625	28.0	116.8
S_{BD}	−423.32713990	997	−35.4	118.8	−424.35178396	723	−30.3	117.7
S_{CD}	−423.32616328	1211	−1.8	57.9	−424.35237695	593	−1.0	55.6
S_{CC}	−423.32730904	960	32.0	0.0	−424.35181726	716	25.2	0.0
S_{DD}	−423.32827568	748	−34.8	0.0	−424.35308390	438	−29.8	0.0
b1	−423.32384930	1719	−0.8	119.6	−424.34979997	1159	−0.4	120.1
b2	−423.32435871	1607	0.1	0.0	−424.35095479	905	0.1	0.0

[a] P = planar structure, S_{xy} = the structure at the saddle point between conformers *x* and *y*, b*n* = the transition structure at the barrier *n*.

TABLE 4: Spectroscopic Transitions (cm^{-1}) for the Isomers of 2-indanol in Its S_0 and $S_1(\pi,\pi^*)$ States[a,b]

	A		B		C		D	
	S_0	S_1	S_0	S_1	S_0	S_1	S_0	S_1
ν_0		37008.4		36953.7		36936.9		36961.2
$\nu_{29}(0-1)$	92 (87)	79.7 (81)	(87)	84.5 (81)	86 (87)	77.0 (76)	90 (84)	88.1 (76)
$\nu_{29}(0-2)$	182	157.9			171	154.1	178	174.1
$\nu_{29}(0-3)$		235.7						
$\nu_{29}(0-4)$		314.9						
ν_{28}	243 (236)	167.7 (136)	(252)	(152)	(230)	166.8 (138)	(247)	(138)
ν_{27}	354 (396)	275.8 (264)	(485)	(256)	366 (338)	273.7 (261)	(490)	(260)
$\nu_{54}(0-1)$	*157* (155)	(117)	(184)	(133)	(155)	(116)	(183)	(115)
$\nu_{54}(0-2)$	313	309.2						
ν_{53}	(302)	(305)	(251)	(250)	281 (273)	318.5 (271)	(255)	274.2 (271)

[a] Numbers in parentheses are calculated frequencies. S_1 calculated frequencies were obtained from CIS/6-311++G(d,p) level of theory. [b] S_0 values in *italics* are from the liquid Raman experiment.

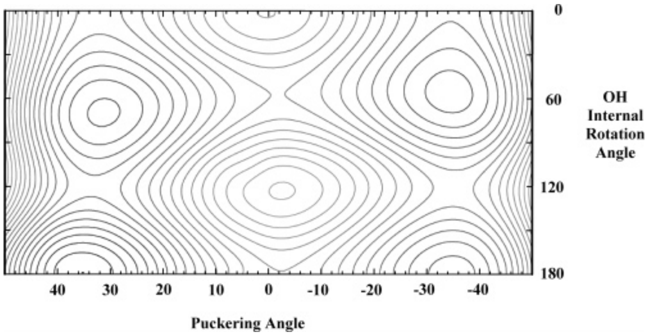


Figure 5. Topological map equivalent to Figure 4.

and interconversion of these conformers. To get accurate results from ab initio calculations, the MP2 theory was used with a large basis set such as triple-ζ or 6-311++G(d,p), and this requires a large amount of computational time. It was also noted that the MP2/6−31(d,p) calculation resulted in different relative energies of the less stable structures as compared to the 6-311++G(d,p) calculation.[11] A basis set which gives more reliable results in terms of energy and structure using a reasonable amount of computation time can be achieved by adding to the MP2/6−31(d,p) basis set a set of diffuse functions to the atoms other than the hydrogens. The role of the diffuse functions is to primarily give more flexibility for the description of the molecular orbitals.[18,19] We found that the results from the MP2/6-31+G(d,p) with the diffuse functions reproduced in a satisfactory way the calculations from the triple-ζ basis set (Table 2). The calculated ring-puckering angles in the four conformers using the 6-31+G(d,p) basis set can be seen to be in excellent agreement with those obtained using the high level theory. The structure of 2-indanol was optimized at different puckering angles using the MP2/6-31+G(d,p) level of theory.

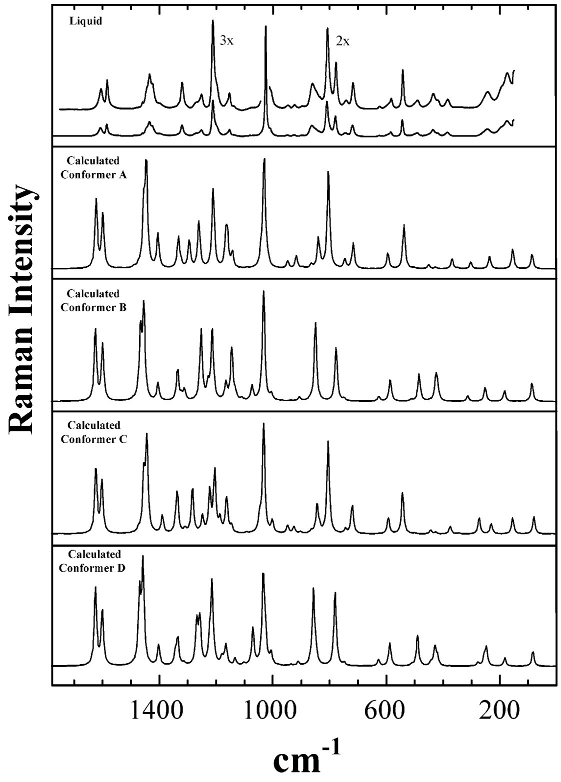


Figure 6. Comparison of the low-frequency liquid Raman spectrum of 2-indanol at 90 °C to the computed spectra of its isomers.

To construct the energy surface representing the effect of the internal rotation and the ring-puckering in 2-indanol, the OH group was allowed to rotate about the C−O bond from a dihedral angle of 0° to 180° at increments of 15°, with the

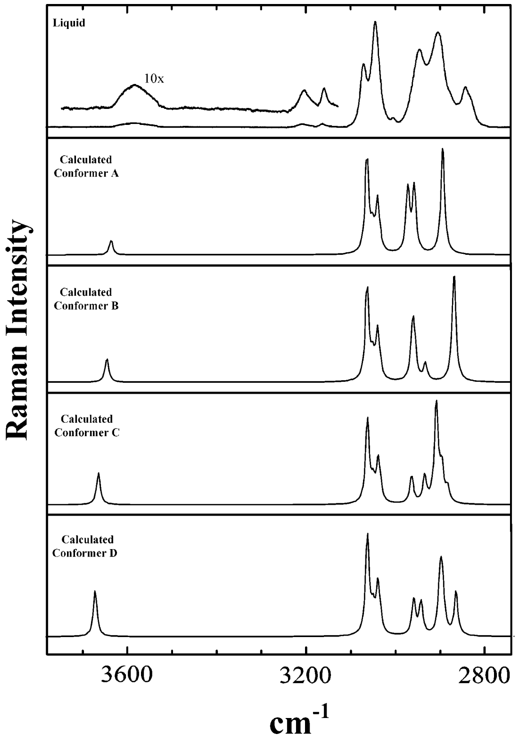


Figure 7. Comparison of the liquid Raman spectrum of 2-indanol at 90 °C to the computed spectra of its isomers for the high-frequency region.

puckering angle being fixed and all the carbon atoms, except the one bonded to the oxygen atom, lying in the plane of the molecule. The internal rotation angle was defined to be 180° for conformer A with the maximum amount of hydrogen bonding to the benzene ring. Figure 3 provides descriptions of the ring-puckering and internal rotation modes along with those for two other lower frequency modes, the ring flapping and ring twisting. A computer program was utilized to interpolate the data points along the puckering angle axes and the OH internal rotation axes to produce the energy surface and contour shown in Figures 4 and 5. To get even more accurate results where the saddle points are, the energy and geometry of the transition structures were calculated using the triple-ζ basis set and the results are shown in Table 3. The detailed calculated structures for the energy map are given in the Supporting Information, Supplementary Tables 1 and 2.

In addition, DFT with the triple-ζ basis set was used to calculate the vibrational frequencies for 2-indanol, and approximate normal mode assignments were made for each conformer by examining the atom vector displacements. These results will be available elsewhere.[20] The motions of the low-frequency modes are shown in Figure 3. We have also calculated the vibrational frequencies in the S_1 state for the most stable structure and compared them with the experimental values.[20]

Spectroscopic Results

Raman and Infrared. A more detailed analysis of the infrared and Raman spectra of IND-ol will be published at a later time.[20] Several of the more important Raman bands are listed in Table 4. Figures 6 and 7 compare the experimental liquid Raman spectra of IND-ol liquid at 90° to the calculated spectrum of the four conformers. Under these conditions a great deal of intermolecular hydrogen bonding between neighboring molecules is expected so the −OH stretching region as well as other −OH vibrations will reflect these interactions. Vapor-phase Raman and infrared studies are underway in order to investigate the independent molecules without the intermolecular interactions. Figures 6 and 7 are primarily intended to demonstrate that on the whole the DFT calculations do a good job of reproducing the spectra.

Laser-Induced Fluorescence (LIF) Spectra. Figure 8 shows the fluorescence excitation spectra of IND-ol along with a number of the assignments. The presence of the four predicted conformers can be seen in the $S_1(\pi,\pi^*)$ excited state. Not only can the four 0_0^0 transitions be observed, but a number of the low-frequency vibrational assignments are shown in the figure. Table 4 lists the excitation frequencies (0_0^0) for the four conformers along with the assignments of several of these modes. The dispersed spectra from the 0_0^0 bands of conformers A, C, and D have also been recorded and these provide data for the S_0 state levels of these molecules. Table 4 summarizes some of these frequencies. It can be noted that the ring-puckering has values of 92, 86, and 90 cm^{-1} for the S_0 states of A, C and D, respectively. The calculated value for B is 87 cm^{-1}. In the

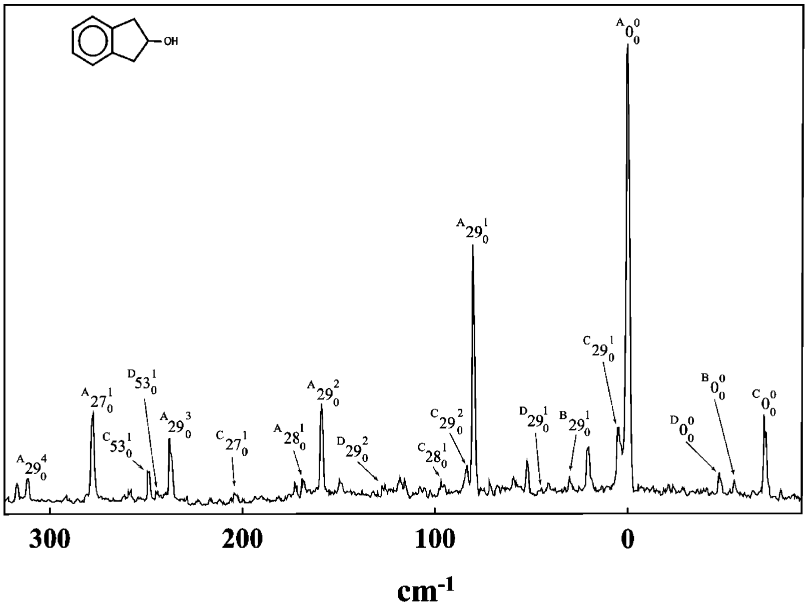


Figure 8. Laser-induced fluorescence excitation spectrum of 2-indanol.

TABLE 5: Populations (in %) of A, B, C, and D Conformers of 2-Indanol in the Electronic Ground State

		calcd MP2/cc-pVTZ		calcd MP2/6-311++G(d,p)	
	expt	25 °C	90 °C	25 °C	90 °C
A	81	76	67	77	70
B	3.1	7.4	10	5.3	7.7
C	11	9.0	12	11	13
D	4.5	7.9	11	6.3	8.9

S_1 states the values are 80 (A), 77 (C), 88 (D), and 85 cm^{-1} (B). Table 4 also shows some of the higher quantum states for the ring puckering and lists values for the flapping (ν_{28}), ring angle bending (ν_{27}), ring twisting (ν_{54}), and the O−H internal rotation (ν_{53}). He and Kang[12] also reported a few of the values we show in Table 4 for the A and C isomers in their S_1 states. For A they report the 0_0^0 band at 37017 cm^{-1} with a puckering frequency of 80 cm^{-1} (82 cm^{-1} calculated). In our work the 0_0^0 is at 37008 and the puckering at 79.7 cm^{-1}. For C their 0_0^0 origin is reported to be at 36948 and the puckering levels at 75 (81 calculated) and 146 cm^{-1} for the 0−1 and 0−2 transitions. In our work the 0_0^0 band is at 36937 cm^{-1} and the puckering levels at 77.0 and 154.1 cm^{-1}.

On the basis of the intensities of the 0_0^0 bands, which are all expected to have very similar transition moments, the distribution of conformers in the S_0 state can be calculated. The distribution can also be calculated based on the theoretical calculations of the energies of the four conformers and based on the assumption that the molecules have not had a chance to equilibrate upon jet-cooling. Table 5 presents these results. The sample before jet-cooling was heated to 90 °C and at this temperature the MP2/6-311++G(d,p) computation leads to a distribution of 70% (A), 8% (B), 13% (C), and 9% (D) vs experimental values of 82, 3, 11, and 5%, respectively. Although the relative energies from the calculations can only be approximate, they do suggest that there has been some sample equilibration upon cooling since experimentally more molecules are observed for the lowest energy conformer A. More importantly, the agreement between the experimental and computational results is highly satisfactory. In the millimeter-wave study mentioned previously,[13] only the principal isomer of 2-indanol had been observed.

Conclusions

Detailed computations have been carried out in order to produce a two-dimensional energy map of 2-indanol in terms of its ring-puckering and −OH internal rotation coordinates. The isomer with intramolecular hydrogen bonding to the benzene ring is calculated to be about 4.6 to 6.3 kJ/mol lower in energy than the three other conformers, which have similar conformational energies. The LIF spectra support these calculations and show evidence for all four isomers. Several of the vibronic bands, including those for the ring-puckering and −OH torsion, have been observed for the different isomers. The distribution of isomers calculated from the FES spectra and the ab initio calculations are in satisfactory agreement.

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Supporting Information Available: Tables of total energies (upper) in hartrees and relative energies (lower) in cm^{-1} calculated from the MP2/6-31+G(d,p) level of theory (the first and second sets). This material is available free of charge via the Internet at http://pubs.acs.org.

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