Rotational Isomers of 1-Methoxynaphthalene: A Combined Study by Ultraviolet Laser Spectroscopy in a Supersonic Jet and ab Initio Theoretical Calculation

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Two rotational isomers of 1-methoxynaphthalene have been identified in the collision-free environment of a supersonic jet expansion by the use of laser-induced fluorescence spectroscopy and photoionization time-of-flight mass spectrometry. In the fluorescence excitation spectra, the features corresponding to the higher-energy conformer are sensitive to conditions of the nozzle expansion, and this has been attributed to a shallow energy minimum of the conformer on the methoxy torsional potential surface. The observations are consistent with the ab initio (HF, MP2//HF, and DFT/B3LYP) theoretical results that in addition to the most stable trans planar conformation, the molecule has a second higher-energy conformer (∼9 kJ/mol) in which the methoxy group is perpendicular to the plane of the naphthalene ring.

1. Introduction

Laser electronic spectroscopy in combination with the supersonic jet expansion technique has emerged in recent years as a powerful tool with which to probe the conformational landscapes of flexible molecules and weakly bound molecular clusters.[1,2] An important feature of the jet expansion process is that if the energy barriers separating the individual conformers are not too low, then the populations of various conformers are frozen out, at least partially, at temperatures significantly greater than the typical terminal temperature attained in a free jet.[3,4] This method has been employed successfully to a broad range of organic molecules and also to biomolecules such as neurotransmitters, amino acids and small peptides, and nucleic acid bases and also to their clusters that include a certain number of water molecules.[1,5−10]

The conformational behavior of aromatic methyl ethers, particularly the energy profile for the internal rotation of the methoxy group with respect to the plane of the aromatic ring, has been studied over the past three decades with methoxybenzene (anisole) serving as the prototype system.[11] Unlike the conflicting conclusions of the experimental studies, theoretical results at different levels of accuracy predict the existence of a stable coplanar geometry and also a nonplanar conformer for the molecule.[11] For example, laser electronic spectroscopy perfomed by Breen et al.[7a] showed that in the ground state anisole exists in only one isomeric form, and their results were in agreement with the conclusion of early gas-phase spectroscopic studies that the molecule has a 2-fold potential barrier for methoxy internal rotation.[12] However, NMR studies showed that the methoxy internal-rotation potential has both 2-fold and 4-fold barriers, which indicated the existence of a second conformer.[13] Recently, electron diffraction studies of Popik, et al.[14] of *o*-chloroanisole showed that in addition to the most stable planar conformation the molecule has a stable second conformer in which the methoxy group is perpendicular to the plane of the benzene ring, in accordance with the results of ab initio quantum chemical calculations.

In this paper, we report the conformational behavior of 1-methoxynaphthalene studied by laser-induced fluorescence (LIF) spectroscopy in a supersonic jet expansion. Ab initio quantum chemical calculations at the HF, MP2//HF, and DFT/B3LYP levels of theory with the 6-31G** basis set have been used to corroborate our experimental findings. Conformations and electronic spectra of the isomeric molecule 2-methoxynaphthalene have been studied recently by Troxler et al. using laser-induced fluorescence spectroscopy in a supersonic jet.[15] Although two conformations corresponding to the two coplanar orientations of the methoxy group with the naphthalene ring (cis and trans) are identified, it has been observed that the molecule exists mostly in the cis form. This preference for the cis form is remarkably different from that of 2-hydroxynaphthalene, where a 2:1 ratio of the cis/trans distribution was reported.[10a] Furthermore, ab initio (HF/ 6-31G**) calculations predicted a third conformer of 2-methoxynaphthalene to exist only ∼1 kJ/mol higher in energy than the trans planar conformer, although no assignment for this conformation was made in the fluorescence excitation spectrum of the jet-cooled molecules.

Conformational characteristics of 1-hydroxynaphthalene have been the focus of a number of recent spectroscopic investigations.[10,16] Hollas and Hussein[16] first showed by using electronic absorption measurements that 1-hydroxynaphthalene exists in the vapor phase in two distinct rotational isomeric forms. Subsequently, Johnson et al.[10a] showed by using rotationally resolved fluorescence spectroscopy under supersonic jet conditions that the two isomers correspond to the two coplanar orientations of the hydroxyl group with respect to the naphthalene ring. The relative intensities of the origin bands of the two isomers in the $S_1 \leftarrow S_0$ absorption spectrum show that the energy difference between them is about 220 ± 50 cm^{-1} (∼3 kJ/mol) in the ground state.[16] This observation is qualitatively in agreement with the ab initio (HF/ 6-31G**) theoretical prediction that the trans isomer is 912 cm^{-1} (10.9 kJ/mol) lower in energy than the cis isomer.[10a] A larger steric interaction of the hydroxyl proton with the hydrogen atom attached to the C8 carbon of the naphthalene ring is commonly used to explain the relative preference of the trans over the cis conformer, although the explanation is not straightforward because the

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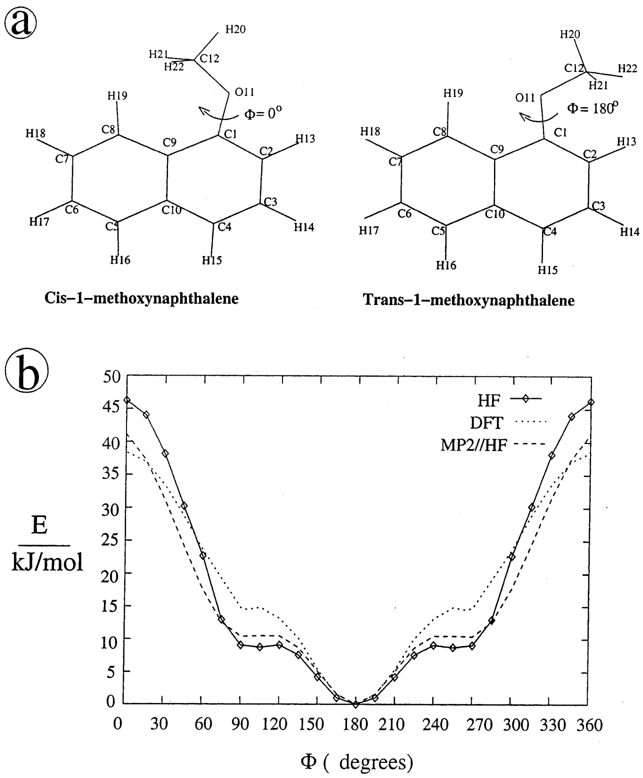

Figure 1. (a) Atom numbering scheme used for the geometry optimization of 1- methoxynaphthalene and (b) potential energy curve of 1-methoxynaphthalene as a function of ϕ as obtained from HF/6-31G** (—), MP2//HF (- -), and DFT/B3LYP (••) calculations.

electronic spectrum further indicates that the order of stability is reversed in the excited state.[10b]

In the case of 1-methoxynaphthalene, the bulkier methoxy group is expected to make the cis isomer energetically less favorable. We provide in this paper experimental evidence and theoretical justification for the existence of a nonplanar conformer in addition to the most stable trans form.

2. Computational Method and Results

Ab initio electronic energies and geometries in the ground state of different conformers of 1-methoxynaphthalene were calculated at the Hatree—Fock (HF) and DFT/B3LYP levels using the Gaussian 94 suite of programs.[17] Figure 1a shows the atom numbering scheme used for the optimization of the molecular geometry.

To estimate the approximate potential energy curve for the internal rotation of the methoxy group with respect to the plane of the naphthalene ring, a series of single-point calculations were performed for different values of the methoxy dihedral angle ϕ ($C_9-C_1-O_{11}-C_{12}$) from 0 to 180° in increments of 15°. In each run, ϕ was kept fixed, and the geometry of the molecule with respect to all other internal coordinates was optimized at both the HF and DFT/B3LYP levels using the 6-31G** basis set. The resulting potential energy curves as a function of ϕ are shown in Figure 1b. The two minima found therein correspond to dihedral angles of 180° (trans planar isomer) and 90° (perpendicular conformer). The former also corresponds to the global minimum of the potential energy surface. The HF potential energy curve (solid line —) shows that the perpendicular conformer ($\phi = 90°$) is ~8.7 kJ/mol higher in energy than the trans planar conformer, and it has a shallow minimum with a well depth of 0.29 kJ/mol (24 cm^{-1}). Single-point calculations at the MP2 level for the HF-optimized geometries using the same basis set confirm the existence of this minimum, and the results are shown in Figure 1b (dashed line - -). The results of the DFT/B3LYP calculations are also in the same line of the HF calculations and are shown in Figure 1b with dotted lines (••), and here the well depth of the shallow minimum is ~28 cm^{-1}.

3. Experimental Section

The experimental setup to measure laser-induced fluorescence excitation and dispersed fluorescence spectra has been described before.[18] Briefly, a gaseous mixture of 1-methoxynaphthalene (obtained from Aldrich, >98% pure) and helium at a pressure of 30 psi is expanded into a vacuum through a pulsed nozzle (General Valve) of orifice diameter 0.5 mm to generate the seeded supersonic expansion. The sample is kept in a glass cell immediately behind the nozzle and maintained at room temperature to keep its vapor pressure at a low level such that cluster formation is avoided. The jet-cooled molecules are excited with the frequency-doubled output of a tunable dye laser (Sirah and Plasma Technik, model: Cobra Stretch) pumped by the second harmonic of a Nd:YAG laser (Spectra Physics, model: INDI). The laser beam intersects the free jet perpendicularly about 12 mm downstream from the nozzle orifice, and the fluorescence is collected from the intersection point in a direction perpendicular to both the laser and the free jet. Fluorescence excitation spectra are measured by detecting the total fluorescence after it passes through an optical glass filter (Hoya Optics UV-34) to eliminate stray light from the laser. A 0.75-m monochromator (Spex, Model 750M) with a grating of groove density 2400/mm is used to measure dispersed fluorescence spectra. The fluorescence is detected using a Hamamatsu R928 photomultiplier tube, and the output signals of the photomultiplier are processed with a boxcar averager (model: SR 250, Stanford Research Corporation). The averaged output of the boxcar is stored in a computer using a homebuilt data acquisition system.

Time-of-flight (TOF) spectra were measured with a homebuilt linear TOF mass spectrometer (Wiley and McLaren design)[19] following the (1 + 1) resonance-enhanced multiphoton ionization (REMPI) of the jet-cooled molecules after passing through a skimmer. The resulting ions are extracted in a field of 120 V/cm and accelerated in the potential field of 350 V/cm between the extraction and ground plates. The length of the flight tube is 65 cm. The mass-resolved ions are detected by a channeltron electron multiplier (Galileo CEM 4039), the output signals are averaged using a digital oscilloscope (Tektronix TDS 380), and the averaged output is recorded in a computer.

4. Results

The low-energy region of the fluorescence excitation spectrum of the $S_1 \leftarrow S_0$ electronic transition of jet-cooled 1-methoxynaphthalene is shown in Figure 2a. The strongest band in the spectrum at 31 685 cm^{-1} is ascribed to the electronic origin (0_0^0) transition of the molecule. The fluorescence excitation spectrum for the same electronic transition ($S_1 \leftarrow S_0$) in 1-hydroxynaphthalene measured under the same conditions of the jet expansion is shown in Figure 2b for comparison. It is identical to what was reported by Lakshminarayan et al.[10b] and also by Johnson et al.[10a] Two strong transitions in the spectrum, one at 31 182 cm^{-1} and the other at 31 456 cm^{-1}, had been ascribed to the electronic origin bands of the cis and trans rotational isomers, respectively. It becomes clear from the two spectra that only one isomeric form of 1-methoxynaphthalene shows up in the excitation spectrum. This observation is consistent with the prediction of our theoretical calculation (see

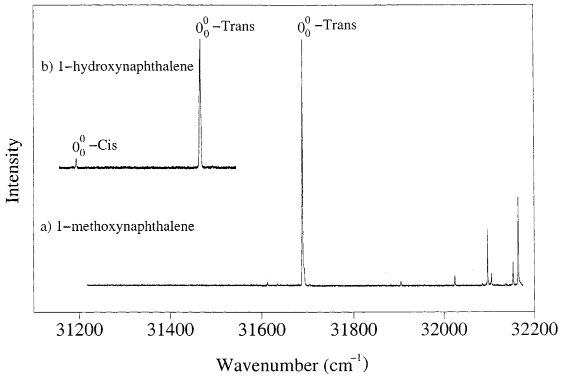

Figure 2. Fluorescence excitation spectra of the jet-cooled (a) 1-methoxynaphthalene and (b) 1-hydroxynaphthalene measured under a He backing pressure of 30 psi.

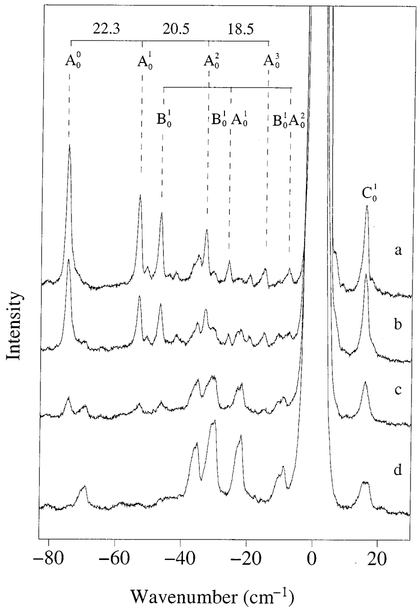

Figure 3. Fluorescence excitation spectra of 1-methoxynaphthalene at different backing pressures of He: (a) 30, (b) 20, (c) 10, and (d) 5 psi.

above) that unlike 1-hydroxynaphthalene, the planar cis isomeric form of 1-methoxynaphthalene is a maximum on the potential energy profile in the ground state. Therefore, we assign the band at 31 685 cm^{-1} in Figure 2a to the electronic origin band of the trans isomer.

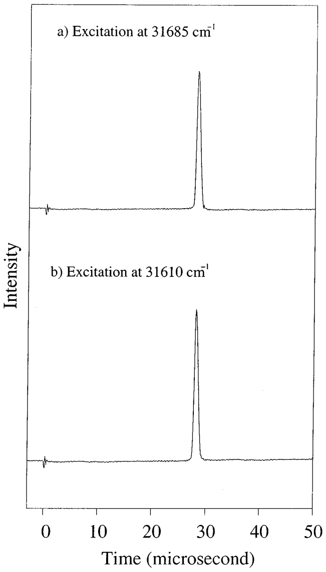

Figure 4. Time-of-flight spectrum of the molecular ions generated by REMPI of 1-methoxynaphthalene for excitation at (a) 31 685 cm^{-1} (electronic origin band of the major conformer) and (b) 31 610 cm^{-1} (the band denoted by A_0^0).

Figure 2a also reveals that a number of weak features also appear around the strong origin band in the fluorescence excitation spectrum. These are magnified and illustrated in Figure 3a. It is observed that the weak features to the red of the origin band form a regular pattern that could be attributed to a progression and combination of two low-frequency vibrations of 22 and 28 cm^{-1}. They are labeled A and B, respectively. To investigate the origin of these spectral features, we have measured the spectra under different expansion conditions by varying the backing pressure of the carrier gas (helium), and these are displayed in Figure 3a−d. It is observed that the transitions on the lower-energy side of the origin band are sensitive to the expansion conditions of the nozzle, but the feature at $0_0^0 + 15$ cm^{-1} (denoted by C_0^1) is present under all of the expansion conditions. The former set of transitions is strong only under higher backing pressures of the carrier gas. As the backing pressure is lowered (i.e., the cooling in the expansion is reduced), the features begin to disappear, and a new set of transitions appear in the same region. These can be ascribed to hot and sequence bands. The same behavior is observed when other carrier gases are used (N_2 and Ar). Therefore, the weak features in Figure 3a are due to neither impurities nor hot bands but are generated in the jet expansion only when the cooling is efficient. One could attempt to assign these to van der Waals clusters of 1-methoxynaphthalene. However, we must add that we have shown recently[20] that the electronic origin band of the dimer is 350 cm^{-1} red-shifted from the monomer origin. Furthermore, pure clusters are known to be formed only at much higher sample vapor pressures than employed in our experiment. Therefore, we conclude that those weaker features are not due to homoclusters of 1-methoxynaphthalene. Another source of these features could be the van der Waals complex with a trace amount of water impurity in the carrier gas. To verify this possibility, we purposely increased the concentration of water vapor in the carrier gas by passing the latter through liquid water heated to different temperatures but found no enhancement in the intensity of these features with increases in the temperature of water. Therefore, we conclude that these are also not due to vdW complexes with water.

To further eliminate the possibility of van der Waals complexes, we have measured the time-of-flight spectrum (Figure 4) of the molecular ions generated by (1 + 1) REMPI with laser frequencies corresponding to the origin band (31 685 cm^{-1}) of the molecule and the weak feature denoted by A_0^0 (31 610 cm^{-1}). The TOF spectrum indicates that the mass of the ion generated from A_0^0 is the same as the molecular mass of 1-methoxynaphthalene. Thus, we assign A_0^0 and the set of weaker cold bands in Figure 3a to a second conformer of 1-methoxynaphthalene. The notable characteristic of this observed conformer is that the fraction of molecules belonging to this conformation is very small when the jet is relatively warm. A detectable amount of the second conformer is generated only when the expansions are carried out using higher backing pressures of the carrier gas. This indicates that the intermolecular collisions during jet expansion transform a fraction of the molecules to this conformer and its population is retained in the collision-free cold environment of the jet. Such behavior has been reported for a conformer of allylbenzene by Philis et al.[21]

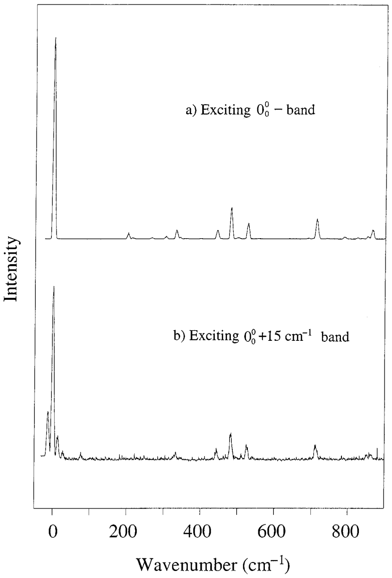

Figure 5. Dispersed fluorescence spectra of 1-methoxynaphthalene for excitation of the (a) 0_0^0 band and the (b) $0_0^0 + 15$ cm^{-1} band of the major conformer.

Figure 5 shows the dispersed fluorescence spectra obtained by exciting the origin band of the major conformer and the blue-shifted feature at $0_0^0 + 15$ cm^{-1} (denoted by $C_0{}^1$ in Figure 3a). In the emission spectrum, the 0_0^0 band is also the strongest transition, and the major vibronic bands within the spectral range shown appear at 336, 450, 486, 531, and 716 cm^{-1}. In comparison, when the $0_0^0 + 15$ cm^{-1} band is excited, the emission intensity at the excitation frequency is very weak, and the strongest transition in the dispersed fluorescence spectrum is shifted by 16 cm^{-1}. This strongest band behaves as a false origin, and all of the major vibronic features observed in the origin-excited emission spectrum (Figure 5a) are built on it with the identical intensities and frequency spacing. Moreover, a short progression of the low-frequency (~16 cm^{-1}) vibration also appears in the spectrum. Therefore, C ($0_0^0 + 15$ cm^{-1}) must be due to a low-frequency vibrational mode in the excited state, and the strongest band at 16 cm^{-1} in the dispersed fluorescence spectrum is a $C_1{}^1$-type transition. Recently, Ichimura et al.[22] have studied the spectroscopy and excited-state dynamics of *o*-, *p*- and *m*-methylanisoles. In the fluorescence excitation spectra of both *o*-(methyl-h_3)-anisole and *o*-(methyl-d_3)-anisole, a weak band is observed at $0_0^0 + 13$ cm^{-1}. The position of the band remained unaffected on deuteration of the methyl group, and this led the authors to assign it to the torsional vibration of the methoxy group. On the basis of similarities in spectral positions, we assign the band at $0_0^0 + 15$ cm^{-1} to one quantum excitation of the torsional motion of the methoxy group with respect to the naphthalene ring. As it appears very weakly in the fluorescence excitation spectrum and does not form a longer progression, the orientation of the methoxy group with respect to the plane of the naphthalene ring and hence the geometry of the molecule must be similar in both the ground and excited states.

Figure 6 shows the dispersed fluorescence spectra obtained by exciting the A_0^0, A_0^1, and B_0^1 bands of the second conformer. The dispersed fluorescence spectrum from the origin band of the main conformer is shown here again to make a comparison. It is observed that the spectra in Figure 6a and d show a striking similarity. The most-intense bands in both spectra appear at the excitation frequencies. Except for the low-frequency features in Figure 6a, the higher-frequency vibronic transitions in the two spectra are identical. The low-frequency transitions in the three spectra (6a–c) can be analyzed as progressions and combinations of two vibrations of fundamental frequencies 22 and 35 cm^{-1}, and these are denoted in the Figure. In Figure 6b, the emission at the excitation wavelength is comparatively weak, and the strongest band appears at 22 cm^{-1}. All of the vibrations appearing in Figure 6a are built on this band, and thus it behaves as a false origin. We assign A_0^0 to the electronic origin band of the second conformer of 1-methoxynaphthalene and A_0^1 to one quantum excitation of a low-frequency (22 cm^{-1}) vibration. Similarly, a dispersed fluorescence measurement by excitation of the $B_0{}^1$ band (28 cm^{-1}) shows that the frequency of the corresponding vibration in the ground state is 35 cm^{-1} (Figure 6c). These low-frequency vibrations must be associated with the large-amplitude internal rotational motions of the methoxy group of the molecule. Without studying a deuterated methoxy compound, definitive assignments as to which frequency corresponds to the methyl internal rotation and which one corresponds to the torsional motion of the methoxy group cannot be made. Nevertheless, the notable point is that unlike the major conformer, the minor conformer shows pronounced activity of the vibrations associated with the methoxy group of the molecule in the fluorescence excitation as well as in the dispersed fluorescence spectra. This indicates that electronic excitation affects the orientation of the methoxy group of the second conformer.

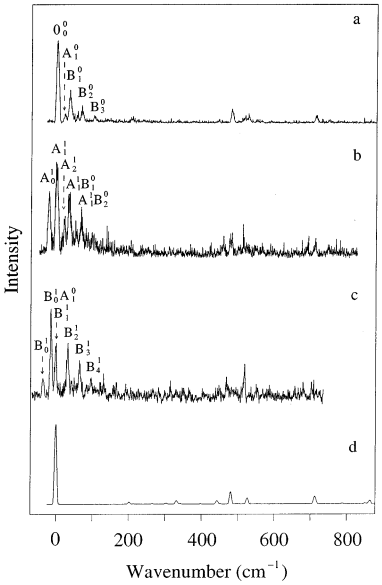

Figure 6. Dispersed fluorescence spectra of the bands denoted by (a) A_0^0, (b) A_0^1, (c) B_0^1 and the (d) 0_0^0 band of the major conformer.

5. Discussion

The results presented in section 4 have clearly indicated that the perpendicular conformer of 1-methoxynaphthalene is generated in the jet only when the expansion is carried out from a high backing pressure of the carrier gas. A likely mechanism of the process is an interconversion between two isomeric forms of the molecule, which corresponds to a collisional transition from the deep minimum to the shallow minimum section of the methoxy torsional potential energy curve (Figure 1b). The reverse of this process, where a high-energy conformer of a molecule undergoes geometry rearrangement to a low-energy form by collisions during jet expansions, has been documented in a number of studies. The phenomenon was studied in the past decade by Gutowsky and co-workers,[3] with various small organic molecules having multiple rotational isomers using Fourier transform microwave spectroscopy. Before that, Felder and Günthard[4] studied the same phenomenon by cryogenic trapping of the conformers of 1,2-difluoro- and 1,2-dichloroethanes and methyl nitrite from an expanded beam in an argon matrix, and the conformational distributions were measured by IR spectroscopy. The crucial molecular parameter that determines the efficiency of the process is the conversion barrier between the initial and the final isomeric forms. The collisions need to have only enough energy to surmount the energy barriers, and the intermolecular interactions between the colliding pairs also contribute to the crossing of the barrier. A gross observation is that a relaxation can occur if the energy barrier is not more than ~10 kJ/mol. The released energy is distributed either internally or given up by the high-energy conformer to the colliding partner and relaxes to a low-energy form.

Our calculations show that the energy barrier separating the two isomeric forms of 1-methoxynaphthalene is ~9 kJ/mol. Therefore, this much energy has to flow to the methoxy internal rotational mode for the interconversion from the planar to the perpendicular form of the molecule to occur. As the gap between successive quanta of the methoxy torsional vibration is small, the mode can effectively exchange energy with the collisions. Furthermore, intermolecular collisions can also induce energy transfer from other vibrational modes populated at room temperature. Figure 3c and d shows that when the backing pressure of the nozzle is low, a large number of hot and sequence bands are observed in the fluorescence excitation spectra. Therefore, in the preexpansion stage, many modes are populated above the zero-point energy level and collisions can induce energy transfer from these vibrations to the methoxy torsional mode, and interconversion occurs when the threshold amount of energy flows to the torsional mode.

It has been mentioned previously that similar behavior has been reported recently by Philis et al.[21] for the higher-energy conformer of allylbenzene in a supersonic jet expansion. The potential energy curve for the internal rotational motion of the allyl group was calculated earlier by Breen et al.[7b] using a molecular orbital−molecular mechanics MOMM-85 program. Two rotational isomers, one corresponding to a deep-minimum potential at the lowest energy and another, to shallow minimum at a higher energy, were predicted. Philis et al.[21] have shown that in the MPI spectrum, the origin band of the higher-energy conformer is visible only when the jet expansions are carried out from high backing pressures of the carrier gases, and the band vanishes when the backing pressure is reduced.

The geometrical parameters obtained from the theoretical calculation (HF/6-31G**) indicate that the prevalence of the trans planar isomer arises from a favorable overlap between a lone-pair orbital on the oxygen and the π orbital of the naphthalene ring. As a result, the $C_1{-}O_{11}$ bond length (1.347 Å) is shorter than the $O_{11}{-}C_{12}$ bond length (1.399 Å). The overlap is reduced when the methoxy group is rotated out of the plane of the naphthalene ring, and this is indicated by the gradual elongation of the $C_1{-}O_{11}$ bond to 1.363 Å in the perpendicular form. However, although the trans geometry is the lowest-energy conformer of the molecule, the calculation shows that there is considerable steric interaction between the methoxy group and the hydrogen atom at the C_2 position in this form. The $C_2{\cdots}C_{12}$ nonbonded distance in the trans configuration (2.81 Å) is much shorter than the sum of the van der Waals radii of the CH and CH_3 groups (4.04 Å).[14] As a result, the angle $\angle C_2{-}C_1{-}O_{11}$ opens up to 124.6°, and $\angle C_9{-}C_1{-}O_{11}$ is squeezed to 114.8° when compared to the ideal value of 120°. For the same reason, the angle $\angle C_1{-}O_{11}{-}C_{12}$ (119.7°) is much larger than the ideal value (109°) for sp^3 hybridization of the oxygen atom. The nonbonding steric interactions are relieved as the methoxy group rotates out of plane. In the perpendicular geometry, the three angles $\angle C_2{-}C_1{-}O_{11}$, $\angle C_9{-}C_1{-}O_{11}$, and $\angle C_1{-}O_{11}{-}C_{12}$ are respectively 120.1, 118.9, and 115.1°. A cancellation of these two opposing factors possibly gives rise to a flat methoxy torsional potential of the perpendicular conformer.

An important distinguishing feature between the spectra of the two conformers is that at least two of the low-frequency vibrations associated with the methoxy group are very active in the fluorescence excitation spectrum of the nonplanar conformer, whereas those vibrations are almost inactive in the planar trans isomer. Our theoretical results provide some hints to a plausible explanation of this behavior. In the planar trans geometry, the $C_1{-}O_{11}{-}C_{12}{-}H_{20}$ dihedral angle is 180°, and two other hydrogen atoms (H_{21} and H_{22}) of the methyl group are dangling out of the plane of the naphthalene ring. As the methoxy group rotates about the $C_1{-}O_{11}$ bond (i.e., as the dihedral angle ϕ changes), the methyl group also rotates about the $O_{11}{-}C_{12}$ bond. Thus, when ϕ is decreased from 180 to 165°, the $C_1{-}O_{11}{-}C_{12}{-}H_{20}$ dihedral angle also changes by 14°. Similarly, when ϕ is 135°, the dihedral angle $C_1{-}O_{11}{-}C_{12}{-}H_{20}$ is 151°. As an oxygen atom is directly linked to naphthalene, a $\pi{-}\pi^*$ electronic excitation in the latter may distort the methoxy torsional angle of the perpendicular conformer and consequently may also induce the torsional motion of the terminal methyl group about the $O_{11}{-}C_{12}$ bond.

6. Summary and Conclusions

Two conformers of 1-methoxynaphthalene have been investigated using laser-induced fluorescence excitation, dispersed fluorescence, and REMPI time-of-flight mass spectroscopic techniques. Ab initio quantum chemical calculations at the HF, MP2//HF, and DFT/B3LYP levels qualitatively support our experimental observations. We hope to measure the rotational band contours of the $S_1 \leftarrow S_0$ origin bands of the two conformers in the near future and obtain further insight into the problem.

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