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Conformational property of ethoxybenzene as studied by laser-jet spectroscopy and theoretical calculations

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Abstract

The conformational property of ethoxybenzene has been investigated by means of the laser-jet spectroscopy and the theoretical calculations.   The quantum-mechanical analysis of the two-dimensional potential surfaces for the S_0 and S_1 states that have been obtained from the DFT and TDDFT calculations, respectively, has been carried out.   Its result suggested the existence of the second conformer (*gauche*) in addition to the main conformer (*trans*) in the both states, and it was predicted that the 0–0 band of the *gauche* conformer would appear at about 400 cm^{-1} lower than that of the *trans* conformer.   The $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled ethoxybenzene has been measured.   The peak that is assignable to the 0–0 band of the second conformer has been observed, whose spectral position (red-shifted from that of the *trans* conformer for about 229 cm^{-1}) is qualitatively consistent with the theoretical prediction.

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1. Introduction

The conformational properties of molecule have been one of the central themes of structural chemistry.   Diffraction and spectroscopic techniques have long been utilized for identification of the stable conformers of gas phase molecules, and recently quantum chemical calculations are thought to be reliable sources to provide information about the number of stable conformers and their energy differences.   However, inconsistent results are sometimes obtained even for the conformational property of relatively simple molecules.   For example, there have been studies with slightly different conclusions as for the existence of the second conformer for α, α, α–trifluoroanisol [1,2].

Ethoxybenzene, the target of the present study, is another example of molecules with inconsistent reports about the conformational property.   A preliminary conformational study of ethoxybenzene by means of gas electron diffraction was first reported in 1993, in which it was concluded that ethoxybenzene exists as a mixture of *trans* and *gauche* conformers (see Fig. 1) in the gas phase [3].   However, two reports have come out recently from independent research groups [4,5], with a conclusion contrarily to that of Ref. [3].   Cinacchi and Prampolini have carried out DFT calculations to make a two-dimensional potential map for the C_{ring}–O and C_{ethyl}–O internal rotation of ethoxybenzene (corresponding to the ϕ_1 and ϕ_2 angles, respectively, shown in Fig. 1) in the S_0 state [4].   Two unique minima, corresponding to the *trans* and *gauche*, seem to exist on their potential surface with the former being more stable. However, they have not mentioned the *gauche* conformer and the quantum-mechanical energy level calculation by using their potential surface have not been carried out. Ramanathan *et al.* have measured the fluorescence excitation and dispersed fluorescence spectra of jet-cooled ethoxybenzene [5].   They have concluded the existence of only one conformer (*trans*) of ethoxybenzene in the gas phase because there was no band assignable to the 0–0 band of the second conformer in their fluorescence excitation

spectrum.   However, the wavenumber range of their measurement was only in the vicinity of the 0–0 band of the *trans* conformer and it does not seem to be wide enough to rule out the possibility of the second conformer.

In the present study, a fluorescence excitation spectrum of jet-cooled ethoxybenzene has been measured with a rather wide wavenumber range.   In addition, theoretical calculations have been carried out to obtain two-dimensional potential surfaces not only for the S_0 state but also for the S_1 state.   Quantum-mechanical energy level calculations have also been carried out to predict the peak positions of the excitation spectrum.   All the experimental and theoretical data have been combined to draw a final conclusion about the existence of the *gauche* conformer of ethoxybenzene.

2. Experimental

A commercial sample (Tokyo Kasei Kogyo Co., Ltd.) with purity better than 99% was used without further purification.   The $S_1 \leftarrow S_0$ fluorescence excitation spectrum was measured by using an apparatus reported previously [6].   The carrier gas used was He and the stagnation pressure was about 2 atm.   The temperature of the sample holder was kept at 263 K in order to obtain the appropriate sample concentration.   The nozzle (General Valve 900 series) was not heated but its temperature rose up to 323 K during the measurement.   The orifice diameter of the nozzle was 0.5 mm.   The jet-expanded sample was irradiated by the UV laser (Lambda-physik, Compex 110 excimer laser and SCANmate 2UV dye laser equipped with an auto-tracking SHG system) at 30 mm downstream of the nozzle outlet.   The applied laser energy was about 150 µJ/pulse. The laser and nozzle systems were driven synchronously at the repetition rate of 30 Hz. The fluorescent light was focused on a Hamamatsu R212 PMT, in front of which cut-off filters (300 nm) were placed.   The output signal from the PMT was processed by a pre-amplifier and a boxcar averager (Stanford Research Systems, SR-250).

3. Theoretical calculations

Program Gaussian 09 [7] was used for all the calculations. In order to obtain the potential map for the electronic ground state (S_0), a series of geometry optimizations were carried out by fixing the internal rotation angles, ϕ_1 and ϕ_2, independently at 0–180° with an interval of 30°. The method used was B3LYP [8,9] with a cc-pVTZ basis set [10]. For the S_1 excited state, the potential map was obtained similarly with the TDDFT method [11-13] and a cc-pVTZ basis set (i.e., TDDFT/B3LYP/cc-pVTZ).

4. Analyses

4.1 Potential surfaces.

The potential energies obtained for the S_0 and S_1 states were fitted to the functional form

$$V(\phi_1, \phi_2) = \sum_{m,n=0}^{6} V_{m,n}^{c} \cos(m\phi_1)\cos(n\phi_2) + \sum_{m,n=1}^{4} V_{m,n}^{s} \sin(m\phi_1)\sin(n\phi_2) \qquad (1)$$

The resultant potential constants, $V_{m,n}^{c}$ and $V_{m,n}^{s}$, are listed in Table 1 and the reproduced potential surfaces are shown in Fig. 2. The potential surface for the S_0 state is essentially the same as that reported by Cinacchi and Prampolini [4], that was obtained by the combination of B3LYP method and a 6-311G(2d, p) basis set. As shown in Fig. 2, there are two unique minima on the potential surfaces both in the S_0 and S_1 states. These two minima correspond to the *trans* ($\phi_1 = 0°$, $\phi_2 = 180°$) and *gauche* ($\phi_1 \approx 0°$, $\phi_2 \approx$ 90°) forms and the former is the global minimum. At the both electronic states, the positions of the *trans* and *gauche* minima are different from each other essentially only in their ϕ_2 values. Full geometry optimizations of the *trans* and *gauche* conformers were carried out for the S_0 and S_1 states. The obtained geometrical parameters are listed in Table 2. The resultant structural parameters show that the S_0–S_1 excitation makes the C–C bonds in the ring longer by 0.01–0.04 Å and C_6–C_1–C_2 and C_3–C_4–C_5 angles larger

by about 4°. In going from the *trans* to *gauche* conformer, the O_7–C_8–C_9 angle becomes larger by about 5° and 3° in the S_0 and S_1 states, respectively. At the both states, the ϕ_2 angle of the *gauche* conformer is not around 60°, the typical value for the *gauche*, but close to 90°.

4.2 Energy level analysis.

The existence of the potential minimum does not mean the existence of the corresponding conformer unless there is at least one energy level with the probability distribution localized on the position of it. As shown in Fig. 2, the overall shape of the potential surfaces for the S_0 and S_1 states are quite different from each other. There is a strong coupling between the ϕ_1 (ethoxy) and ϕ_2 (ethyl) internal rotations in the S_0 state. On the other hand, the coupling is much weaker in the S_1 state. In the S_0 state, the $\phi_2 = 180°$ cross section of the potential surface has its minima at $\phi_1 = 0°$ and 180°. On the $\phi_2 = 0°$ cross section, however, the positions of the minima shifts to $\phi_1 = 90°$ and 270°. Therefore, if the molecule carries out the ethyl internal rotation along with the minimum-energy path starting at $(\phi_1, \phi_2) = (+270°, 0°)$ toward $\phi_2 = 360°$, the ϕ_1 angle changes by $-180°$ ($\phi_1 = +270°$ to $+90°$, see the dashed line in Fig. 2). That is, a half internal rotation of the ethoxy group takes place during a full internal rotation of the ethyl group. In such a case, it is not appropriate to treat the ethoxy and ethyl internal rotations separately by using a one-dimensional potential function for each. Therefore, the energy level calculations were carried out by means of the two-dimensional Hamiltonian [14],

$$H = -\begin{pmatrix} \dfrac{\partial}{\partial \phi_1} & \dfrac{\partial}{\partial \phi_2} \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} \\ B_{12} & B_{22} \end{pmatrix} \begin{pmatrix} \dfrac{\partial}{\partial \phi_1} \\ \dfrac{\partial}{\partial \phi_2} \end{pmatrix} + V(\phi_1, \phi_2) \tag{2}$$

where the elements, B_{11}, B_{12} and B_{22}, in the kinetic energy term were approximated by the following expansion:

$$B_{i,j}(\phi_1, \phi_2) = \sum_{m,n=0}^{4} B_{i,j}^{c\ m,n} \cos(m\phi_1)\cos(n\phi_2) + \sum_{n=1}^{4} B_{i,j}^{s\ 2,n} \sin(2\phi_1)\sin(n\phi_2),$$

$$(i, j = (1,1),\ (1,2),\ (2,2))$$ (3)

The expansion coefficients, $B_{i,j}^{c\ m,n}$ and $B_{i,j}^{s\ 2,n}$, were functions of moment of inertia of the molecule and internal rotors, and they were evaluated by using a method similar to that described in Ref. [15].

The products of free rotation eigenfunctions, $\exp(ik\phi_1)\exp(il\phi_2)/2\pi$, for $k, l =$ −40 to +40 were used as a basis set in order to calculate the energy levels and the corresponding wave functions by means of the matrix diagonalization. The probability distribution was calculated for each of the obtained energy levels by using their wave functions. Then the energy levels whose distribution is localized in the vicinity of the optimized ϕ_1, and ϕ_2 values for the *gauche* form (see Table 2) were assigned to that of the *gauche* conformer. Examples of the probability distribution for some of the energy levels for the S_0 state are shown in Fig. 3.

For the S_0 state, the lowest energy level assignable to the *gauche* conformer was found at 589 cm^{-1} higher than the lowest energy level of the *trans* conformer. On the other hand, the corresponding energy difference for the S_1 state is 184 cm^{-1} (see Fig. 4). Therefore, it was expected that the 0–0 band of the *gauche* conformer would be observed at 405 cm^{-1} red-shifted from that of the *trans* conformer.

5. Results and discussions

Figure 5 shows the observed fluorescence excitation spectrum of ethoxybenzene. The 0–0 band of the *trans* conformer is observed at 36,375 cm^{-1}, almost the same position as reported in Ref. [5]. The peak at 36,541 cm^{-1} (0–0 band +166 cm^{-1}) has been assigned in Ref. [5] to the vibronic fundamental band (C–O–C in-plane bending) of the *trans* conformer on the basis of the dispersed fluorescence spectra and the theoretical calculation. At higher wavenumber range, many other vibronic bands can be observed,

whose assignments are out of the scope of the present study. At the lower-wavenumber side of the 0–0 band of the *trans* conformer, a very weak peak is found at 36,146 cm^{-1} (–229 cm^{-1} from the *trans* 0–0 band). The position of this peak is out of the wavenumber range of the fluorescence excitation spectrum shown in Ref. [5]. As the intensity of this peak relative to the other peaks is almost unchanged even under a poor supersonic jet condition at which some hot band peaks appear, this peak does not seem to be a hot band of the *trans* conformer. No other peak was observed down to about 35,400 cm^{-1} under a cold jet condition. Therefore it is concluded that the peak at 36,146 cm^{-1} is the 0–0 band of the second conformer (*gauche*) of ethoxybenzene. This conclusion (the existence of the *gauche* conformer) is qualitatively consistent with the present theoretical potential energy surface and with the result of the preliminary gas electron diffraction study reported previously [3]. As described in the Section 4, the 0–0 band of the *gauche* conformer was supposed to be red-shifted by about 400 cm^{-1} from that of the *trans* conformer. However, the actual amount of the red-shift is found to be 229 cm^{-1}. This discrepancy can be attributed to the limited accuracy of the theoretical potential surface, especially that for the S_1 state.

Acknowledgements

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Table 1

Potential constants for the internal rotations of ethoxybenzene estimated by the least squares fitting on the potential energies obtained from the B3LYP/cc-pVTZ and TDDFT/B3LYP/cc-pVTZ calculations (in cm^{-1})

	S_0 state (B3LYP/cc-pVTZ)	S_1 state (TDDFT/B3LYP/cc-pVTZ)
Parameters [a]		
$V^c_{0,0}$	1598.1	1931.9
$V^c_{0,1}$	997.7	863.4
$V^c_{0,2}$	362.1	346.9
$V^c_{0,3}$	303.8	183.4
$V^c_{0,4}$	-52.7	-36.9
$V^c_{0,5}$	-11.8	-8.1
$V^c_{0,6}$	2.7	0.8
$V^c_{2,0}$	-101.5	-1216.0
$V^c_{2,1}$	489.4	465.0
$V^c_{2,2}$	254.9	254.2
$V^c_{2,3}$	103.3	-2.0
$V^c_{2,4}$	-80.2	-61.2
$V^c_{2,5}$	-26.9	-25.2
$V^c_{2,6}$	3.7	2.4
$V^c_{4,0}$	7.6	400.8
$V^c_{4,1}$	25.3	-26.1
$V^c_{4,2}$	51.0	42.4
$V^c_{4,3}$	114.2	73.4
$V^c_{4,4}$	-62.3	-63.0
$V^c_{4,5}$	-24.0	-29.2
$V^c_{4,6}$	6.4	8.8
$V^c_{6,0}$	-4.3	-86.6
$V^c_{6,1}$	-5.7	6.3
$V^c_{6,2}$	-5.6	-2.6

$V^{c}_{6,3}$	10.6	15.0
$V^{c}_{6,4}$	-10.6	-20.2
$V^{c}_{6,5}$	-5.6	-12.4
$V^{c}_{6,6}$	2.5	1.7
$V^{s}_{2,1}$	-380.9	-450.4
$V^{s}_{2,2}$	-284.6	-315.9
$V^{s}_{2,3}$	-165.6	-15.6
$V^{s}_{2,4}$	98.3	70.5
$V^{s}_{4,1}$	-38.9	37.9
$V^{s}_{4,2}$	-52.6	-27.0
$V^{s}_{4,3}$	-114.5	-46.7
$V^{s}_{4,4}$	70.2	61.0

[a] See Eq. 1 for the definition of the potential constants.

Table 2

Geometrical parameters and energies of *trans* and *gauche* conformers of ethoxybenzene obtained from the B3LYP/cc-pVTZ and TDDFT/B3LYP/cc-pVTZ calculations

Parameters [a]	S_0 state (B3LYP/cc-pVTZ)		S_1 state (TDDFT/B3LYP/cc-pVTZ)	
	trans	*gauche*	*trans*	*gauche*
Bond lengths / Å				
$C_1–C_2$	1.395	1.395	1.418	1.421
$C_2–C_3$	1.393	1.393	1.424	1.423
$C_3–C_4$	1.386	1.387	1.413	1.412
$C_4–C_5$	1.394	1.393	1.408	1.408
$C_5–C_6$	1.384	1.384	1.423	1.423
$C_6–C_1$	1.398	1.398	1.420	1.417
$C_1–O_7$	1.362	1.363	1.347	1.348
$O_7–C_8$	1.426	1.428	1.437	1.436
$C_8–C_9$	1.514	1.520	1.512	1.520
$C_2–H_{10}$	1.079	1.079	1.077	1.077
$C_3–H_{11}$	1.082	1.082	1.079	1.079
$C_4–H_{12}$	1.081	1.081	1.082	1.083
$C_5–H_{13}$	1.082	1.082	1.079	1.079
$C_6–H_{14}$	1.081	1.081	1.078	1.079
$C_8–H_{15}$	1.095	1.089	1.092	1.089
$C_8–H_{16}$	1.095	1.093	1.092	1.088
$C_9–H_{17}$	1.091	1.092	1.090	1.091
$C_9–H_{18}$	1.090	1.090	1.089	1.090
$C_9–H_{19}$	1.090	1.089	1.089	1.089

Bond angles / °

C₆–C₁–C₂	119.6	119.4	123.1	123.1

C_6–C_1–C_2 119.6 119.4 123.1 123.1
C_1–C_2–C_3 119.5 119.6 117.6 117.3
C_2–C_3–C_4 121.0 121.0 119.5 119.8
C_3–C_4–C_5 119.1 119.0 122.5 122.5
C_4–C_5–C_6 120.6 120.6 118.9 118.6
C_5–C_6–C_1 120.1 120.3 118.3 118.6
C_2–C_1–O_7 124.5 125.2 122.9 123.3
C_6–C_1–O_7 115.8 115.4 114.0 113.6
C_1–O_7–C_8 119.1 120.4 121.4 122.2
O_7–C_8–C_9 107.7 112.7 107.8 111.1
C_1–C_2–H_{10} 121.0 121.1 121.4 121.8
C_3–C_2–H_{10} 119.5 119.2 120.9 120.8
C_2–C_3–H_{11} 119.0 118.9 120.3 120.1
C_4–C_3–H_{11} 120.0 120.0 120.2 120.0
C_3–C_4–H_{12} 120.4 120.5 118.6 118.6
C_5–C_4–H_{12} 120.4 120.5 118.9 119.0
C_4–C_5–H_{13} 120.0 120.1 120.4 120.6
C_6–C_5–H_{13} 119.4 119.4 120.7 120.8
C_5–C_6–H_{14} 121.4 121.3 122.9 122.8
C_1–C_6–H_{14} 118.5 118.4 118.8 118.6
O_7–C_8–H_{15} 109.8 104.3 108.7 104.1
O_7–C_8–H_{16} 109.8 110.2 108.7 109.8
C_9–C_8–H_{15} 110.8 110.2 111.6 110.7
C_9–C_8–H_{16} 110.8 111.6 111.6 112.3
H_{15}–C_8–H_{16} 107.9 107.4 108.4 108.6
C_8–C_9–H_{17} 110.0 109.9 109.6 109.4
C_8–C_9–H_{18} 110.7 110.3 110.9 110.7
C_8–C_9–H_{19} 110.7 111.9 110.9 110.8
H_{17}–C_9–H_{18} 108.5 108.3 108.4 108.4
H_{17}–C_9–H_{19} 108.5 108.2 108.4 108.7
H_{18}–C_9–H_{19} 108.4 108.2 108.5 108.7

Dihedral angles / °

C_6-C_1-C_2-C_3	0.0	-0.3	0.0	-1.3
C_1-C_2-C_3-C_4	0.0	0.2	0.0	2.7
C_2-C_3-C_4-C_5	0.0	-0.0	0.0	-1.3
C_3-C_4-C_5-C_6	0.0	-0.1	0.0	-1.5
C_4-C_5-C_6-C_1	0.0	-0.0	0.0	2.8
C_5-C_6-C_1-C_2	0.0	0.2	0.0	-1.4
O_7-C_1-C_2-C_3	180.0	179.0	180.0	178.5
O_7-C_1-C_6-C_5	180.0	-179.1	180.0	178.7
C_2-C_1-O_7-C_8 (ϕ_1)	0.0	1.7	0.0	-1.7
C_6-C_1-O_7-C_8	180.0	-179.0	180.0	178.2
C_1-O_7-C_8-C_9 (ϕ_2)	180.0	82.2	180.0	90.8
C_6-C_1-C_2-H_{10}	180.0	179.5	180.0	174.1
O_7-C_1-C_2-H_{10}	0.0	-1.2	0.0	-6.0
C_4-C_3-C_2-H_{10}	180.0	-179.6	180.0	-172.8
C_1-C_2-C_3-H_{11}	180.0	-180.0	180.0	-178.8
C_5-C_4-C_3-H_{11}	180.0	-179.8	180.0	-179.8
C_2-C_3-C_4-H_{12}	180.0	179.9	180.0	178.7
C_6-C_5-C_4-H_{12}	180.0	-180.0	180.0	178.5
C_3-C_4-C_5-H_{13}	180.0	-180.0	180.0	179.7
C_1-C_6-C_5-H_{13}	180.0	179.9	180.0	-178.4
C_4-C_5-C_6-H_{14}	180.0	-179.8	180.0	-174.6
C_2-C_1-C_6-H_{14}	180.0	180.0	180.0	176.2
O_7-C_1-C_6-H_{14}	0.0	0.6	0.0	-3.7
C_1-O_7-C_8-H_{15}	-59.2	-158.2	-58.9	-150.0
C_1-O_7-C_8-H_{16}	59.2	-43.2	58.9	-34.0
O_7-C_8-C_9-H_{17}	180.0	176.3	180.0	176.1
O_7-C_8-C_9-H_{18}	60.1	56.9	60.3	56.6
O_7-C_8-C_9-H_{19}	-60.1	-63.5	-60.3	-64.1

Energy

| E / E_h | -386.23274 | -386.23008 | -386.05175 | -386.05083 |
| ΔE^b / cm^{-1} | 0.0 | 583.2 | 0.0 | 204.2 |

[a] See Fig. 1 for the atom numbering.

[b] $\Delta E = E\,(gauche) - E\,(trans)$.

Figure captions

Fig. 1   Molecular models and atom numberings of the *trans* and *gauche* conformers of ethoxybenzene.   The internal rotation angles, ϕ_1 and ϕ_2, are defined as $\phi_1 = \phi(C_2–C_1–O_7–C_8)$ and $\phi_2 = \phi(C_1–O_7–C_8–C_9)$.

Fig. 2   Potential surfaces for the S_0 and S_1 states of ethoxybenzene obtained from the B3LYP/cc-pVTZ (S_0) and TDDFT/B3LYP/cc-pVTZ (S_1) calculations.   See Fig. 1 for the definitions of ϕ_1 and ϕ_2.   The contour interval is 200 cm^{-1}.   The dashed lines on the S_0 potential surface are the minimum-energy paths for the ϕ_2 (ethyl) internal rotation.

Fig. 3   Some examples of the contour plot of the probability distribution for the ϕ_1 (ethoxy) and ϕ_2 (ethyl) internal rotations of ethoxybenzene for the S_0 state.   See Fig. 1 for the definitions of ϕ_1 and ϕ_2.   Energy value for each level measured from the global potential minimum as well as the assignment for the conformer and the vibrational quantum number is shown.

Fig. 4   Vibrational energy levels for the ϕ_1 (ethoxy) and ϕ_2 (ethyl) internal rotations of ethoxybenzene for the S_0 and S_1 states.

Fig. 5 $S_1 \leftarrow S_0$ fluorescence excitation spectrum of jet-cooled ethoxybenzene.   The upper scale shows the excess energy measured from the 0–0 band of the *trans* conformer appearing at 36375 cm^{-1}.
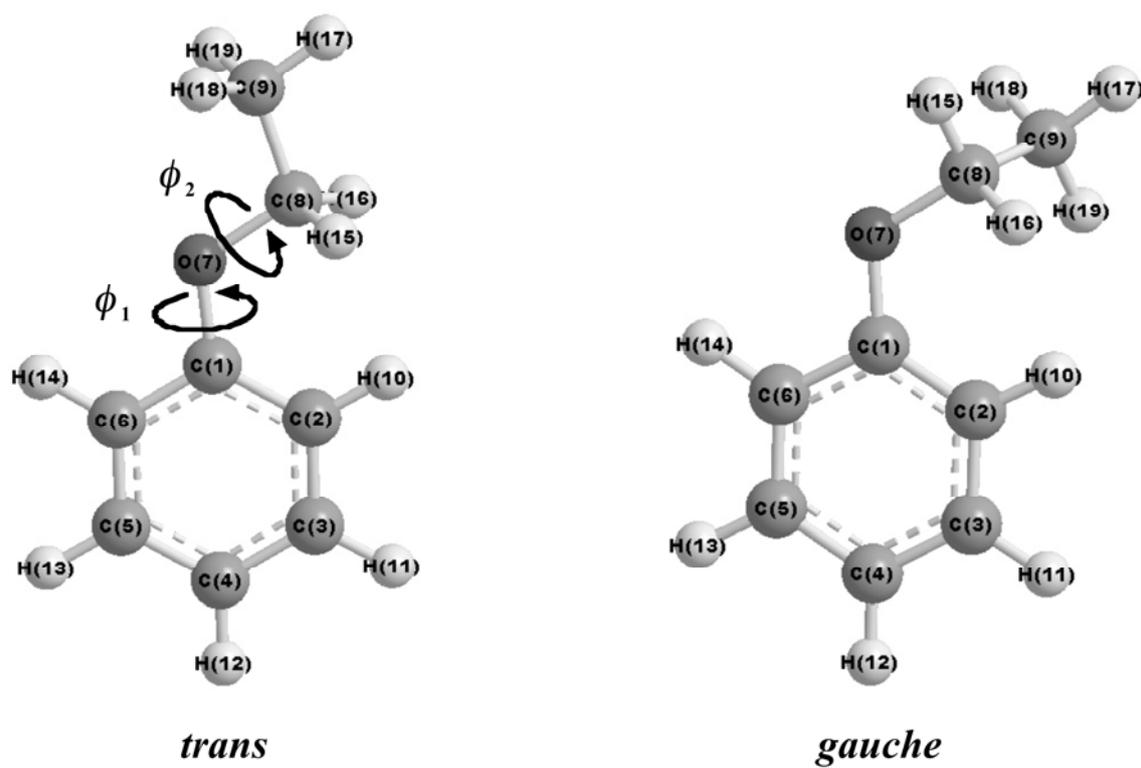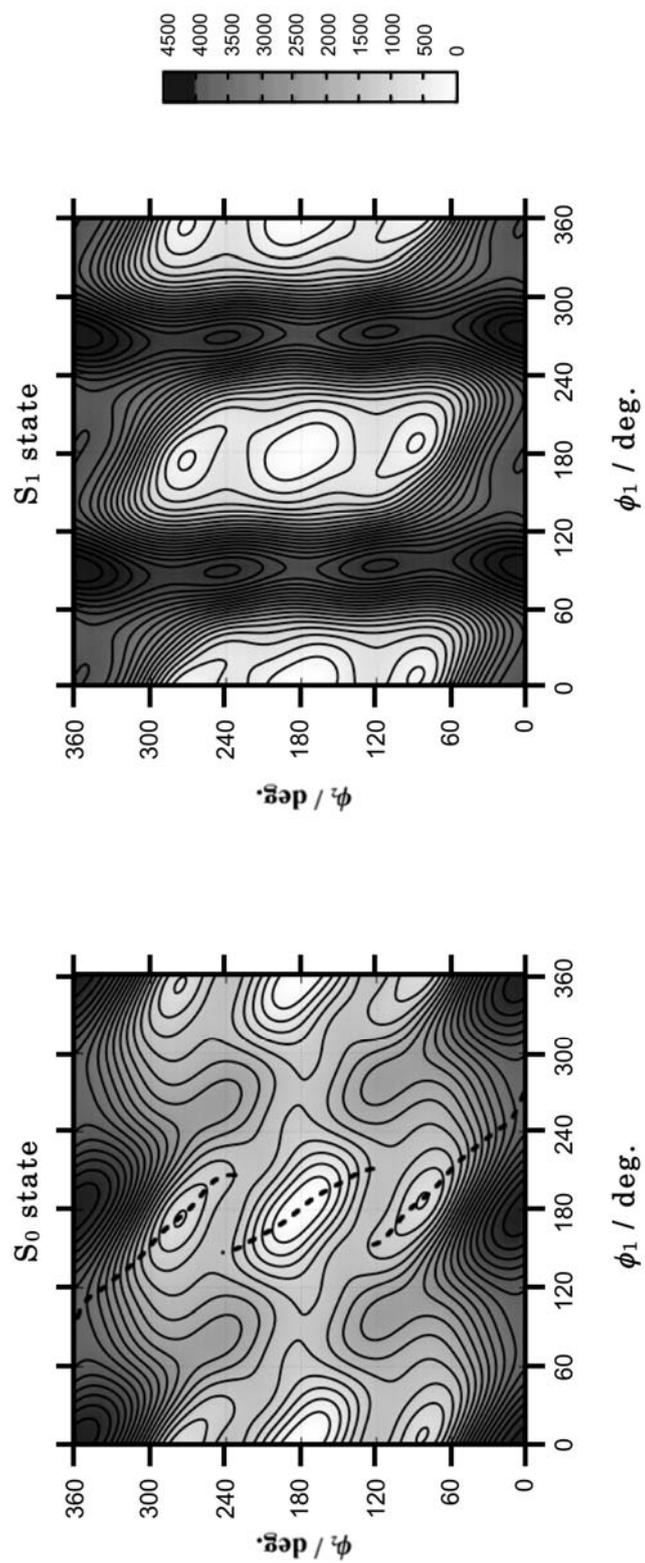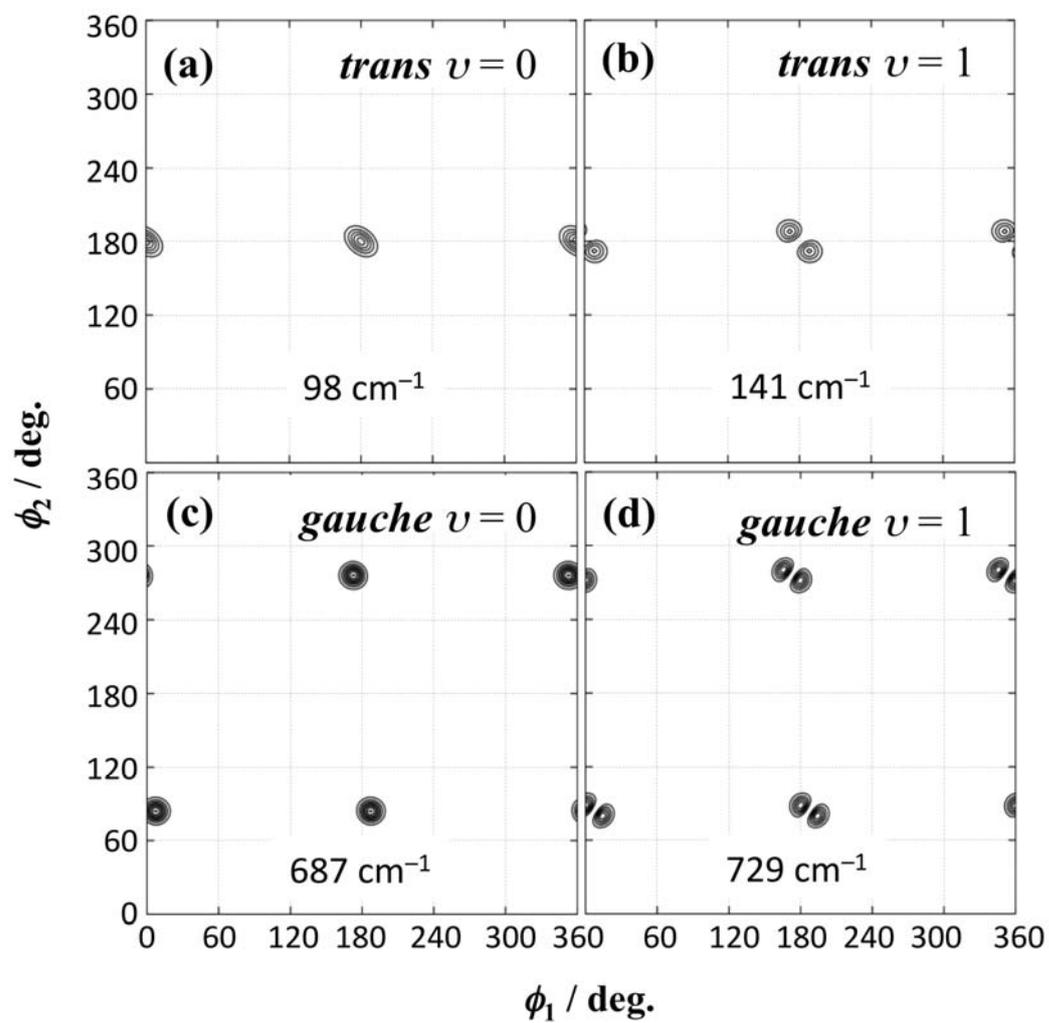
Figure 1

trans   *gauche*

Figure 2

Figure 3

Figure 4

Figure 5

wavenumbers / cm⁻¹