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International Journal of Mass Spectrometry 221 (2002) 107–115

International Journal of Mass Spectrometry

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A REMPI investigation of the minimum energy conformations of diphenyl ether

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Received 1 February 2002; accepted 19 August 2002

Abstract

The structure and low-frequency vibrations of jet-cooled molecules of diphenyl ether are studied with the resonance-enhanced two-photon ionization technique. The origin for the $S_1 \leftarrow S_0$ transition is assigned at 35,873 cm^{-1} and, within 400 cm^{-1}, the vibrational progressions suggest the existence of different conformations proposed for this molecule. A potential energy surface for the ground state, obtained with the use of group theory, is checked against the conformational energy surface given by molecular mechanics simulations. (Int J Mass Spectrom 221 (2002) 107–115)

Keywords: Conformational analysis; Diphenyl ether; Photoionization; Group theory

1. Introduction

The studies of conformational and internal rotation characteristics of bridged-phenyl molecules Ph_2X like, for example, stilbene (X = CH=CH), diphenylamine (X = NH) and diphenylether (X = O) have gathered the attention of many chemists [1–10] interested in the description of the dynamical processes of such compounds. From the investigations on diphenylether (DPE), a floppy molecule, concerning the preferable conformations it was concluded that the planar configuration corresponds to the highest energy conformation. There are four well-defined conformations proposed for DPE (see Fig. 1).

These conformations vary in the angles between the planes of the phenyl rings with one another and with the C–O–C ether plane. The energy differences between the conformations are brought about by the balance between electronic stabilization and steric repulsion. Experimentally, those studies were carried out in the liquid and solid phases and the obtained spectra show inhomogeneous broadening and vibrational congestion. Environmental effects from the complex interactions of the molecule with the solvent also bring additional difficulties on the interpretation of the results.

These restraints were removed as we studied in the gas phase isolated molecules seeded in a supersonic expansion and probed the low-frequency motions in an electronically excited state, using a high resolution laser system. The reduction of spectral congestion due to the expansion cooling resulted in sharp, well resolved features which allow the identification of different stable conformers. We performed a conformational

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1387-3806/02/$ – see front matter
PII S1387-3806(02)00910-7

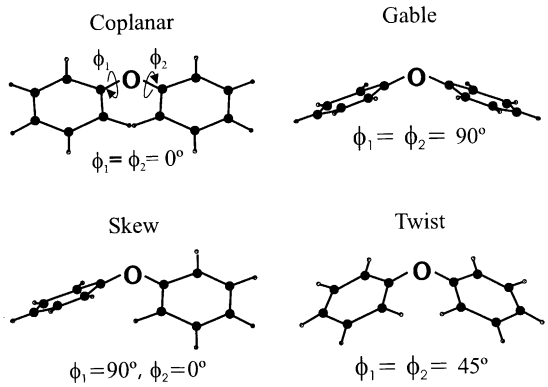

Fig. 1. Schematic diagram of the diphenyl ether molecule. The rotation of the phenyl rings is specified by the internal coordinates ϕ_1 and ϕ_2.

analysis for the ground state by calculating the potential energy as a function of the torsion angles ϕ_1 and ϕ_2 with a molecular mechanics (MM) method. A two-dimensional potential energy surface calculated with an analytical expression from a Fourier expansion was compared to the MM.

2. Experimental

The frequency-doubled output light of a Nd:YAG laser (Quanta Ray DCR-3) pumps a tunable dye laser (Spectra Physics PDL3) that gives pulses of 6 ns width which are frequency-doubled in a β-BaB_2O_4 crystal. The bandwidth of this system is estimated to be 0.15 cm^{-1}. To separate and isolate the second harmonic we use a set of Pellin-Broca prisms. The dye used for excitation and ionization is rhodamine 575 and, after frequency-doubling, the photon energies cover a range from 4.40 to 4.55 eV. Samples were heated at ≈40 °C and a pulsed supersonic valve from R.M. Jordan (model C-211) was used to entrain the vapor in Ar at 1.0 bar (1.0×10^5 Pa) and expand it into the vacuum of the ionization chamber. The expansion jet is intersected at right angles by the laser beam, 80 mm downstream of the nozzle, where the pressure in the source is typically 10^{-5} Pa. Sample molecules are rotationally and vibrationally cooled due to collisions with the argon atoms during the adiabatic expansion. The duration of the jet pulse is approximately 50 μs. The diameter of the nozzle opening is 350 μm. A skimmer with an opening diameter of 1 mm is used at a distance of 20 mm from the nozzle.

Laser energies for the UV light are typically between 50 and 300 μJ after passing a Newport 935-3-OPT high-power/UV-variable attenuator with an attenuation range up to 25 dB. A focus size smaller than 150 μm is obtained with a lens of 16 cm focal length.

The ions created by two-photon resonance-enhanced ionization are separated by a Bruker–Franzen reflectron time-of-flight mass spectrometer and the ion current is amplified by a Johnston MM-1 electron multiplier. The resultant signal is recorded by a fast digitizer (LeCroy 9450). A Stanford Research Systems DG 535 delay/pulse generator is used to trigger the oscillator and the Q-switch of the Nd:YAG laser and the pulsed gas valve.

3. Results

3.1. Spectra of diphenyl ether

Fig. 2 displays the lowest 400 cm^{-1} of the mass resolved excitation spectrum of DPE obtained by collecting the ion signal at mass 170 as the laser wavelength is scanned. The origin transitions for three conformers are the transitions from the ground state (S_0) to the lowest vibrational level in the electronically excited state (S_1). This low energy vibration corresponds to a hindered rotation of the phenyl groups relative to the ether plane. The lowest energy feature is found at 35,873 cm^{-1} and is assigned to the electronic origin. In order to determine if the clearly resolved features arise primarily from cold isolated DPE molecules, or from hot-band transitions, or from van der Waals clusters with the carrier gas, we proceeded as follows.

Attempts were made to reduce the cooling efficiency by changing the stagnation pressure and varying the delay between the pulsed valve and the firing of the Nd:YAG laser; however, these didn't bring any

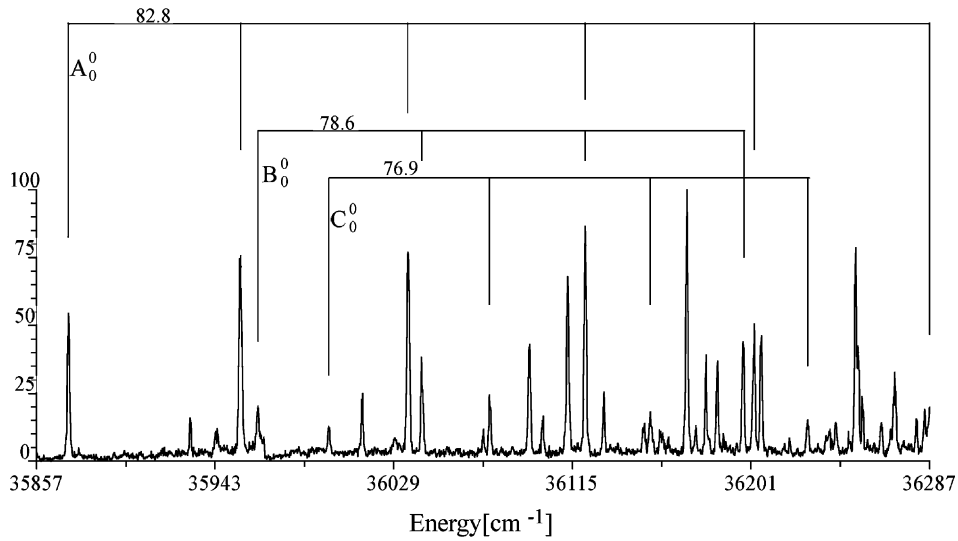

Fig. 2. Resonant two-photon ionization spectrum of DPE from 35,857 to 36,287 cm^{-1}. The supersonic expansion used argon as the carrier gas at a backing pressure of 1.0 bar. The electronic origin is assigned to the peak at 35,873 cm^{-1}. The spectrum was recorded by collecting the ion signal at mass 170 as the dye laser wavelength was scanned.

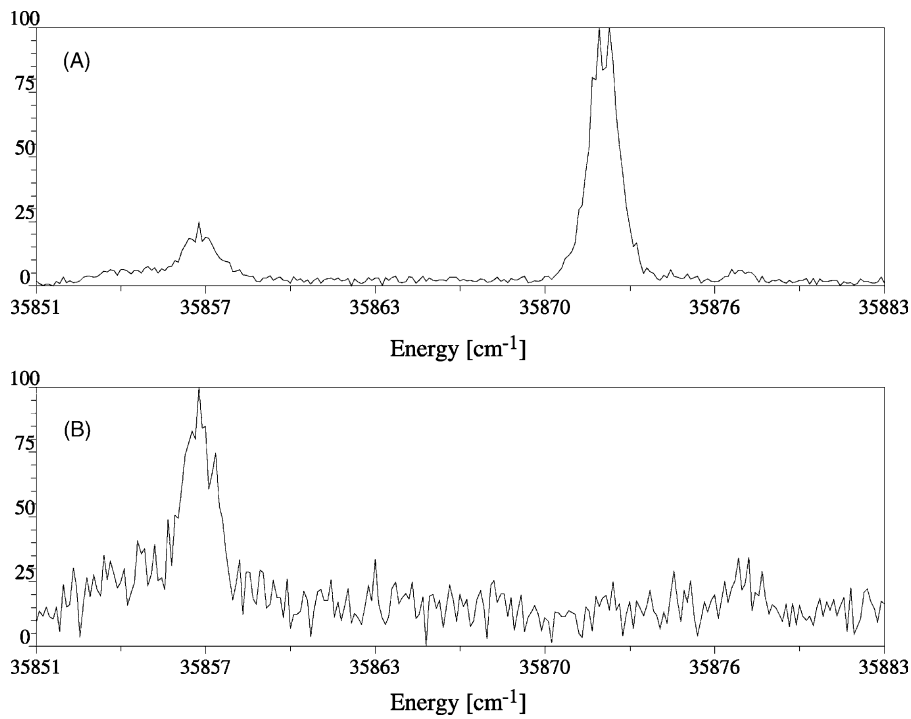

Fig. 3. Wavelength scan around the electronic origin. (A) A scan monitoring ion mass 170 shows a small peak at 35,857 cm^{-1}. In order to know if this feature arises from isolated DPE molecules or from van der Waals molecules a scan monitoring ion mass 210 (Ar–DPE complex) was performed in (B). Since there is no resonance at the electronic origin, that peak is a fragmentation product from the cluster resonance at 35,857 cm^{-1}.

evidence for hot-band transitions. For a van der Waals complex to contribute to the MRES, it would have to fragment to form a signal at $m/z = 170$. Collecting the ion signal at $m/z = 210$ (Ar–DPE cluster) and scanning the excitation laser we get information of possible resonances of that complex. Fig. 3A shows a scan around the electronic origin where the frequencies are corrected for the refractive index of the air. Indeed, the small peak at 35,857 cm^{-1} for ion at $m/z = 170$ is a fragment product originating from $m/z = 210$ as denoted by its resonance at that energy and not seen at the origin frequency 35,873 cm^{-1} (Fig. 3B). After having ruled out the contributions from van der Waals clusters and the hot bands, the vibrational progressions can be assigned based on the origin of transitions for different conformers (see Table 1).

3.2. Phenyl torsions

Diphenyl ether is a non-rigid molecule with large amplitude movements which account for the conversion between isoenergetic configurations. The spectroscopic features of this molecule can be explained using group theory of non-rigid molecules [13].

Considering the two-fold rotational properties of each phenyl ring, the equivalence of the rotors and the invariance of the energy with respect to a simultaneous exchange of the sense of the rotations, the restricted non-rigid group takes the form

$$G_{\mathrm{rNRG}} = [C_2 \times C_2'] \times [W \times V], \quad (1)$$

where $\times$ indicates direct product. The C_2 and C_2' are the two-fold rotation subgroups of each rotor and W and V are, respectively, the exchange and double switch subgroups characterized by

$$C_2 = [\mathcal{E} + \mathcal{C}_2], \quad (2)$$

$$W = [\mathcal{E} + \mathcal{W}], \quad (3)$$

$$V = [\mathcal{E} + \mathcal{V}], \quad (4)$$

where the operators $\mathcal{E}$, $\mathcal{C}_2$, $\mathcal{W}$ and $\mathcal{V}$ are defined as

$$\mathcal{E} f(\phi_1, \phi_2) = f(\phi_1, \phi_2), \quad (5)$$

$$\mathcal{C}_2 f(\phi_i) = f(\phi_i + \pi), \quad (6)$$

Table 1
Transitions in the excitation spectrum of diphenyl ether[a]

Transition frequency (cm^{-1})	Vibrational energy (cm^{-1})[b]	Assignment
35873	0	A_0^0
35931	58.5	
35944	70.7	
35956	82.8	$A_0^1(A_0^0 + 82.8)$
35964	91.1	B_0^0
35998	125.6	C_0^0
36014	141.4	$82.8 + 58.5$
36036	163.2	A_0^2
36043	169.7	$B_0^1(B_0^0 + 78.6)$
36072	199.6	$82.8 + 2 \times 58.5$
36075	202.5	$C_0^1(C_0^0 + 76.9)$
36095	221.7	$82.8 + 78.6 + 58.5$
36101	228.2	
36113	239.9	$82.8 + 2 \times 78.6$
36121	248.3	A_0^3, B_0^2
36130	257.5	$82.8 + 3 \times 58.5$
36150	276.8	$82.8 + 76.9 + 2 \times 58.5$
36153	279.7	C_0^2
36170	297.5	$82.8 + 2 \times 78.6 + 58.5$
36175	301.7	$2 \times 82.8 + 76.9 + 58.5$
36180	306.6	$3 \times 82.8 + 58.5$
36185	312.1	$78.6 + 4 \times 58.5$
36188	314.8	$82.8 + 78.6 + 2 \times 58.5$
36197	324.5	B_0^3
36203	329.7	A_0^4
36206	333.1	$2 \times 78.6 + 3 \times 58.5$
36228	355.4	C_0^3
36237	364.3	$3 \times 82.8 + 2 \times 58.5$
36239	366.2	$4 \times 76.9 + 58.5$
36242	369.1	$76.9 + 5 \times 58.5$
36248	375.1	$82.8 + 5 \times 58.5$
36251	378.5	$82.8 + 3 \times 78.6 + 58.5$
36253	380.1	
36255	381.7	$2 \times 82.8 + 2 \times 78.6 + 58.5$
36264	390.9	$2 \times 78.6 + 4 \times 58.5$
36268	395.4	$82.8 + 78.6 + 4 \times 58.5$
36270	397.2	$82.8 + 4 \times 78.6$
36281	407.7	7×58.5
36285	411.7	$3 \times 78.6 + 3 \times 58.5$
36287	414.0	A_0^5

[a] The frequencies are corrected for the refractive index of the air.

[b] Measured relative to origin at 35,873 cm^{-1}.

$$\mathcal{W}f(\phi_1, \phi_2) = f(\phi_2, \phi_1), \tag{7}$$

$$\mathcal{V}f(\phi_1, \phi_2) = f(-\phi_1, -\phi_2). \tag{8}$$

The final result is a group of order 16, $\mathcal{G}_{16}$, with no correspondence in the theory of point groups. The character table for this group presents 16 non-degenerate irreducible representations.

The potential energy functions for internal rotations are usually expressed as a product of free rotor functions [14]:

$$\begin{aligned} V(\phi_1, \phi_2) = \sum_I \sum_J (&A_{IJ} \cos I\phi_1 \cos J\phi_2 \\ &+ B_{IJ} \cos I\phi_1 \sin J\phi_2 \\ &+ C_{IJ} \sin I\phi_1 \cos J\phi_2 \\ &+ D_{IJ} \sin I\phi_1 \sin J\phi_2). \end{aligned} \tag{9}$$

Applying the projector technique to each term in the expansion (Eq. (9)) we get the basis functions of the irreducible representations of the group that contains all the symmetry elements that convert any DPE conformation into all equivalent conformations:

$$\mathcal{P}_j = \frac{1}{16} \sum_R^{16} \mathcal{X}_j(R)\mathcal{R}, \tag{10}$$

where $\mathcal{X}_j(R)$ is the character corresponding to a symmetry operation $\mathcal{R}$. Amongst the unnormalized functions we get when both I and J are multiples of 2 ($I = 2k$ and $J = 2l$) a totally symmetric representation:

$$\mathcal{X}_{A_1A_1} = \begin{cases} \cos 2k\phi_1 \cos 2l\phi_2 + \cos 2l\phi_1 \cos 2k\phi_2, \\ \sin 2k\phi_1 \sin 2l\phi_2 + \sin 2l\phi_1 \sin 2k\phi_2. \end{cases} \tag{11}$$

From this representation we can write the potential function as a linear combination of the symmetry basis vectors. This leads to

$$\begin{aligned} V(\phi_1, \phi_2) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} [&V_{ckl}(\cos 2k\phi_1 \cos 2l\phi_2 \\ &+ \cos 2l\phi_1 \cos 2k\phi_2) \\ &+ V_{skl}(\sin 2k\phi_1 \sin 2l\phi_2 \\ &+ \sin 2l\phi_1 \sin 2k\phi_2)]. \end{aligned} \tag{12}$$

We may recognize immediately that the energy is constant, with respect to a simultaneous change of the sense of the rotation, due to the non-existence of odd terms in the expansion. We will use an approximation keeping just the terms with $k, l = 0, 1$ (its validity will be checked later):

$$\begin{aligned} V(\phi_1, \phi_2) = &2V_{c00} + V_{c10}(\cos 2\phi_1 + \cos 2\phi_2) \\ &+ V_{c01}(\cos 2\phi_2 + \cos 2\phi_1) \\ &+ V_{c11}(\cos 2\phi_1 \cos 2\phi_2 \\ &+ \cos 2\phi_1 \cos 2\phi_2) \\ &+ V_{s11}(\sin 2\phi_1 \sin 2\phi_2 \\ &+ \sin 2\phi_1 \sin 2\phi_2), \end{aligned} \tag{13}$$

and, for convenience, we take

$$V_{c00} = \tfrac{1}{2}V_0, \qquad V_{c10} = V_{c01} = \tfrac{1}{2}V_2,$$
$$V_{c11} = \tfrac{1}{2}V_{12}, \qquad V_{s11} = \tfrac{1}{2}V_{12'}.$$

Thus, the potential function takes the form

$$\begin{aligned} V(\phi_1, \phi_2) = &V_0 + V_2(\cos 2\phi_1 + \cos 2\phi_2) \\ &+ V_{12} \cos 2\phi_1 \cos 2\phi_2 \\ &- V'_{12} \sin 2\phi_1 \sin 2\phi_2, \end{aligned} \tag{14}$$

where the constant term V_0 is a scale factor, V_2 affects the barrier to internal rotation and V_{12} and V'_{12} are, mainly, constants to shape the potential energy wells. Smeyers [19] has called the term in V'_{12} the "cog-wheel" effect because it reflects the energy change if the rotors move together or in opposite senses.

Introducing the symmetry coordinates:

$$\mathcal{S}_1 = \tfrac{1}{2}(\phi_1 + \phi_2), \tag{15}$$

$$\mathcal{S}_2 = \tfrac{1}{2}(\phi_1 - \phi_2), \tag{16}$$

the potential energy expression becomes

$$\begin{aligned} V(\mathcal{S}_1, \mathcal{S}_2) = &\tfrac{1}{2}V_0 + 2V_2 \cos 2\mathcal{S}_1 \cos 2\mathcal{S}_2 \\ &+ \tfrac{1}{2}V_{12}(\cos 4\mathcal{S}_1 + \cos 4\mathcal{S}_2) \\ &- \tfrac{1}{2}V'_{12}(\cos 4\mathcal{S}_1 - \cos 4\mathcal{S}_2). \end{aligned} \tag{17}$$

4. Discussion

A way to assign features in an electronic spectrum, due to different conformations of the molecule, is to check for different responses to power saturation [15]. The intensity difference of two lines in the spectrum, involving transitions from a common initial state, is due to different transitions strengths (Franck–Condon factors). As the power is increased the stronger line will saturate first, and the relative intensity of the weaker line will increase. When different initial states are involved we have two possibilities: if it is just a matter of different Franck–Condon factors, the behavior with the laser power will follow the pattern described above; but if there is a difference in population of the initial levels (different conformations) in the limit of saturation, the two lines will still have different intensities. Assuming the frequency for the 0–0 band to be at 35,873 cm^{-1}, denoted as A_0^0 in Table 1, the second member of the progression for this conformer A is 82.8 cm^{-1} higher. Similarly, for conformers B and C, the difference between the second and the first term of the progressions give the vibration frequencies 78.6 and 76.9 cm^{-1}, respectively. The feature at 58.5 cm^{-1} may be identified either with a torsion mode or a ring flap mode. According to previous studies for biphenylic compounds [16–18], active modes falling in the 60 cm^{-1} range have been considered a consequence of torsional motion. In our measured spectra there is no manifestation of a progression having 58.5 cm^{-1} as a fundamental mode and without further studies, we can not disregard the ring flap possibility. Besides the three well distinctive progressions the assignment of almost all of the left transitions may be credited to overtone and combination bands. The peaks at 70.7, 228.2 and 380.1 cm^{-1} remained unidentified.

The intensity pattern of the frequency progressions at 82.8, 78.6 and 76.9 cm^{-1}, based on the origin transitions for different conformers, indicates that DPE undergoes some change in the coordinates of these vibrations upon electronic excitation. In fact, the envelope of the torsional progressions suggests that the transition from the minimum of the potential curve in the ground state to the minimum in the excited state is not the most probable one. Nonetheless, the absence of extensive progressions implies some similarity in both ground and excited potential surfaces. Moreover, the anharmonicities shown in the torsional spacings indicate that in a double-potential well model for the excited state the barrier should not be too high.

A picture for the ground state potential surface may be obtained by molecular mechanics (MM) calculations. The MM program used here is PCMODEL [11]. This program makes use of the molecular mechanics approximation where a molecule's energy is taken as the sum of several contributions, including those due to bond streching, bond bending, van der Waals attractions and repulsions between non-bonded atoms, electrostatic interactions due to polar bonds and energy changes accompanying internal rotation about single bonds. The equilibrium geometry is reached by letting the molecule relax to its energy minimum.

In Fig. 4 the conformational energy surface for the ground state of DPE is represented as a contour map in the intervals $0^\circ \leq \phi_1 \leq 180^\circ$, $0^\circ \leq \phi_2 \leq 180^\circ$.

Four distinct conformations can be identified: (1) the coplanar structure, with both phenyl rings and the C–O–C triangle in the same plane, has an energy 6.7 kcal/mol ($\sim$2300 cm^{-1}) above the minimum; (2) the "gable" conformation, when both phenyl rings are perpendicular to the C–O–C plane ($\phi_1 = \phi_2 = 90^\circ$), has a relative energy of 1.6 kcal/mol ($\sim$549 cm^{-1}); (3) in the "skewed" conformation the two phenyl rings are in orthogonal planes to each other ($\phi_1 = 90^\circ, \phi_2 = 0^\circ$) and have an energy of 0.4 kcal/mol ($\sim$136 cm^{-1}) above the minimum; (4) the minimum energy conformation, "twisted," is found at $\phi_1 = \phi_2 = 45^\circ$.

The high energy of the coplanar conformation can be seen as arising from the repulsion between the ortho hydrogen atoms. On the other hand, the change in energy going from the "twist" to the "skew" forms is very small. There is a stabilization due to the conjugation of the π-electrons upon the oxygen atom with one of the phenyl rings but, probably, the skew form has a steric hindrance between the ortho hydrogen atom inside the C–O–C angle and the opposite phenyl ring. Apparently, in the "gable" conformation the conjugation of oxygen with the phenyl rings is not very strong.

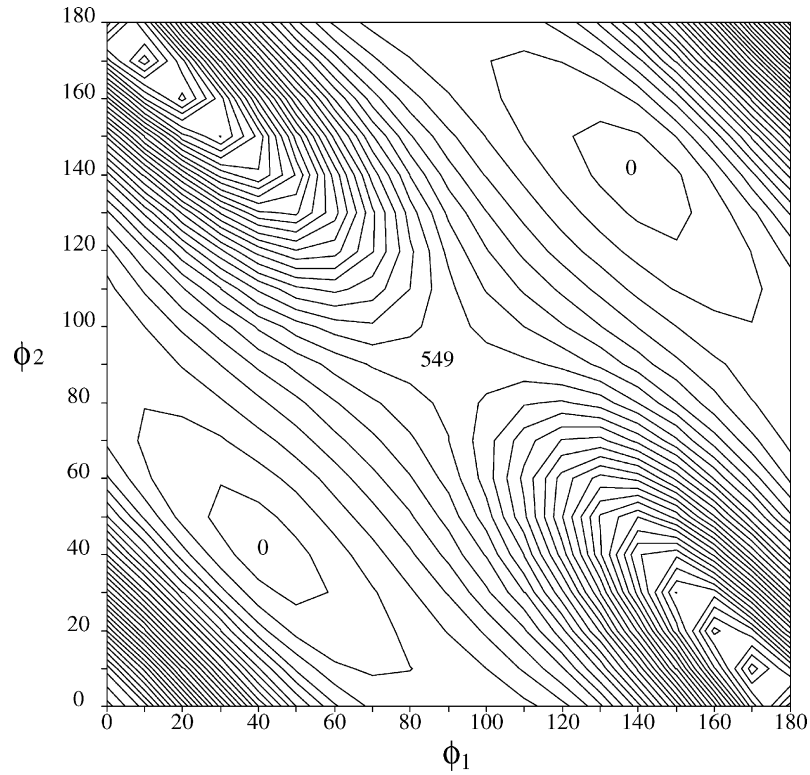

Fig. 4. Molecular mechanics conformational energy map for DPE in the ground electronic state. Energy values on the contours are in kcal/mol and angle values are in degrees. For a definition of angles ϕ_1 and ϕ_2 see Fig. 1.

It is worth noticing the low energy region surrounding the minimum. The flatness and size of that region give information of how populated that conformer is at room temperature. According to Ruoff et al. [12], due to the rapid cooling in the adiabatic expansion, the equilibrium concentrations of the different conformers at the temperature of the valve before expansion are preserved if the barrier to internal rotation is greater than about 1.1 kcal/mol ($\sim$400 cm^{-1}). From Fig. 4 we infer that interconversion between equivalent minima may occur involving transition states around the $\phi_1 = 90^\circ, \phi_2 = 0^\circ$ form, with an activation energy of 0.4 kcal/mol. Transition states with a "gable" structure would need about 1.6 kcal/mol which make them less probable paths for interconversion. Using the energy values for the conformations, as given by MM, and fitting in Eq. (14) we have obtained, as potential energy parameters for the two-dimensional surface in

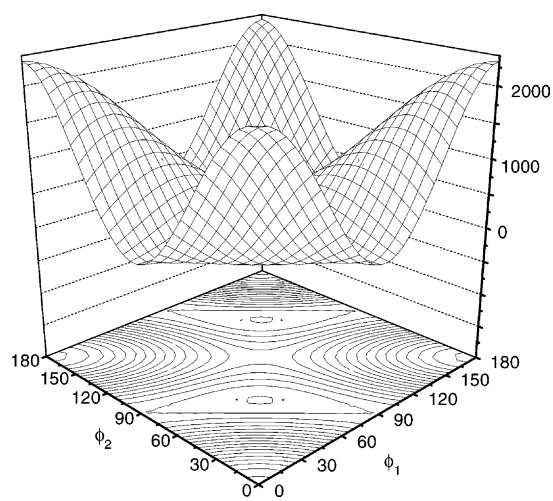

Fig. 5. Simulated two-dimensional potential energy surface for the phenyl torsions of the S_0 state of DPE. The lower contour closely resembles the MM conformational map output.

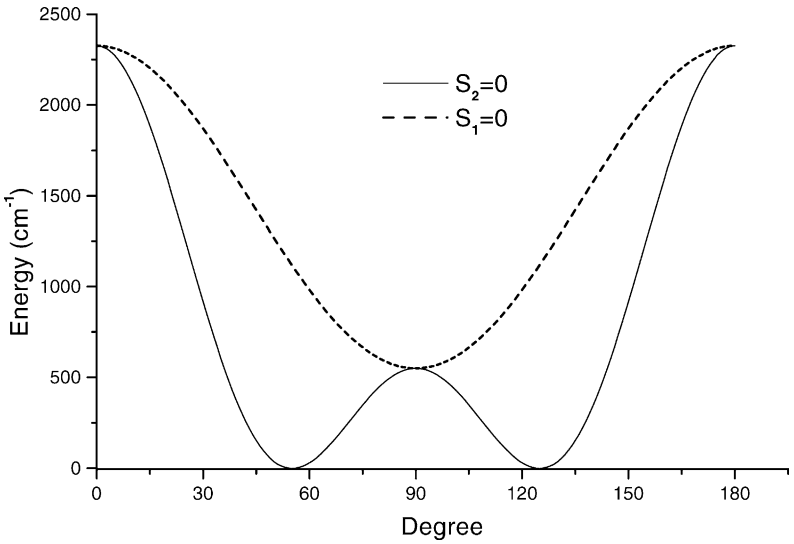

Fig. 6. Potential energy surfaces for in-phase (solid line) and out-of-phase torsions (dashed line).

the S_0 state, the following values:

$$V_0 = 787, \qquad V_2 = 444,$$
$$V_{12} = 651, \qquad V'_{12} = -635\,\mathrm{cm}^{-1}.$$

In Fig. 5 the corresponding two-dimensional potential energy surface and respective contour are displayed. The phenyl torsion analysis, described earlier, gave for the ground state potential surface an energy minimum for the torsion angles $\phi_1 = \phi_2 = 55^\circ$ which are a bit higher than the region minimum ($40^\circ \leq \phi_1, \phi_2 \leq 45^\circ$) found with MM.

Fig. 6 shows slices of the potential energy surface of Fig. 5 taken along the diagonals, which means variation along the symmetry coordinates $\mathcal{S}_1$ and $\mathcal{S}_2$. The in-phase ($\mathcal{S}_2 = 0$) and out-of-phase ($\mathcal{S}_1 = 0$) torsions exhibit quite different curves. The in-phase torsion shows a steeper wall and is expected to correspond to a higher frequency. But both indicate $2326\,\mathrm{cm}^{-1}$ as the energy value for the barrier to simultaneous phenyl torsion. Assuming that the potential surface for the excited state wouldn't change dramatically, according to the absence of extense progressions, we may say that the in-phase torsion is responsible for the $82.8\,\mathrm{cm}^{-1}$ fundamental and the out-of-phase ring torsion for either the 78.6 or the $76.9\,\mathrm{cm}^{-1}$ modes. The fact that the two conformations A and B have a common band at $248.3\,\mathrm{cm}^{-1}$ may indicate a chance of interconversion between them and which we know is possible between the "twisted" and the 'skewed' forms. Accordingly, conformer C is attributed to the "gable" configuration.

5. Conclusion

We have examined the vibrational progressions of the high resolution spectrum of jet-cooled molecules of diphenyl ether and assigned the origin at $35{,}873\,\mathrm{cm}^{-1}$. Most of the spectrum features were identified and the intensity pattern shows three distinctive progressions based on different conformers.

The potential barriers for internal rotation of the phenyl rings have been determined for the ground state and a two-dimensional potential surface shows an energy minimum in good agreement with the literature but higher than the one obtained with the group theory treatment of the phenyl torsions. This difference is, probably, due to the fact that we didn't take the C–O–C angle in account.

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