THE METHYL AND METHOXYL TORSIONAL MODES AND THE LATFICE VIBRATIONS IN THE LOW-FREQUENCY RAMAN SPECTRUM OF 1,4-DIMETHOXYBENZENE

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ABSTRACT

The low-frequency $(10-450 \text{ cm}^{-1})$ Raman spectra of solid (at 300 K and 130 K) and liquid (at 335 K) 1,4-dimethoxybenzene- d_0 and 1,4-dimethoxybenzene- d_5 have been measured. The methyl and methoxyl torsional transitions have been identified and the corresponding torsional barriers calculated. Upon deuteration the methyl torsional barrier is reduced by 450 cm⁻¹, implying a coupling between the methyl torsion and a low-frequency ring mode. As far as the torsions are considered, the internal dynamic situation in 1,4-dimethoxybenzene resembles that in axisole. A tentative assignment of the observed lattice bands is given. Certain changes in the spectrum when going from the solid to the melt are attributed to the coexistence of both *cis* and *trans* conformers in the liquid state.

INTRODUCTION

In previous reports from this laboratory [1-4] we have examined the lowfrequency vibrational spectra of anisole, guaiacol and veratrole and their deuterated analogues. In these studies the methyl and methoxyl corsions were identified and the corresponding torsional barriers were calculated. In the past, numerous reports have been devoted to the "restricted rotation" in 1,4-dimethoxybenzene. Measurements of dielectric relaxation times have been made using various solvents and different sample temperatures [5-23] resulting in qualitative estimates of the contribution of group rotation to the overall relaxation. In addition vibrational spectra [5, 8, 23], ¹³C MMR relaxation data [23], and high resolution solid state ¹³C NMR spectra [24, 25] have been presented, yet no direct observation of the methyl torsional mode has been reported. Experimental information about the low-frequency torsional modes is relatively scarce in general but of importance both for the characterization of the potential energy hypersurface and the force field of the molecule. The low-frequency part of the vibrational spectrum also provides information about the separability of internal and external modes, and the coupling between translational and rotational lattice vibrations [26]. In the present study we therefore report low-frequency Raman spectra of

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1,4-dimethoxybenzene and give assignments for the methyl and methoxyl torsions confirmed by deuteration.

EXPERIMENTAL

1.4-Dimethoxybenzene- d_0 (Fluka AG, purum) was purified by sublimation at 0.15 Torr and 50°C. 1,4-Dimethoxybenzene- d_6 was prepared by methylation of hydroquinone (Merck AG, fotopur) in 20% NaOH solution with dimethyl sulphate- d_6 (Merck AG, degree of deuteration 99%). Optimum yield of 1,4-dimethoxybenzene- d_6 was obtained with 1.25 mol of dimethyl sulphate- d_6 per mol hydroquinone. Column chromatography, (Kieselgel 60, Merck AG) eluting with a mixture of 70% cyclohexane and 30% accorded and sublimation was used to isolate and purify the product. The low-frequency Raman spectra were measured as described previously [27]. Spectra of solid state samples were measured using 180° excitation. Spectra of the melt were obtained with 90° excitation and a single-pass cuvette, situated in an oven-type heater.

CALCULATIONS

The crystal structure of 1,4-dimethoxybenzene has been determined by Goodwin and co-workers [28] and discussed by Kitaigorodskii [29]. The molecules are incorporated into the crystal lattice in the symmetric *trans* form. The reduced moments of inertia of the methyl and methoxyl tops were calculated using the molecular geometry given in ref. 28 and the expression given by Pitzer and Gwinn [30]. The torsional barriers were calculated from the observed torsional transitions by solving the Mathieu equation numerically as described previously [27].

RESULTS AND DISCUSSION

The low-frequency Raman spectra of 1,4-dimethoxybenzene- d_0 and 1,4-dimethoxybenzene- d_6 , measured at different conditions are displayed in Figs. 1 and 2, and the assignments of the torsional modes are given in Table 1 together with the calculated barriers.

In the spectrum of 1,4-dimethoxybenzene- d_0 a broad asymmetric band, centered at about 280 cm⁻¹ is observed. After cooling the sample to 130 K two distinct bands were resolved, (c.f. Fig. 1(a) and 1(b)). Deconvolution of the asymmetric band in the spectrum measured at 300 K revealed the components at 280 cm⁻¹ and 264 cm⁻¹. In the spectrum of 1,4-dimethoxybenzene- d_6 two broad bands are observed at 245 cm⁻¹ and 160 cm⁻¹. We assign the bands at 280 cm⁻¹ and 245 cm⁻¹ to the δ (C--C) mode for 1,4-dimethoxybenzene- d_0 and $-d_6$ respectively. This assignment agrees with the results of Hester et al. [31] who, from a normal coordinate analysiz, obtained a potential energy distribution for this mode corresponding to 65% of ring (CCCC) torsion (cf. also ref. 32). The bands at 264 cm⁻¹ and 160 cm⁻¹ we assign to



Fig. 1. Comparison of the low-frequency Raman spectra of 1,4-dimethoxybenzene- d_c and 1,4-dimethoxybenzene- d_c : (a) 1,4-dimethoxybenzene- d_o , solid at 300 K, slit 2.5 cm⁻¹, 2 × 10³ counts s⁻¹; (b) 1,4-dimethoxybenzene- d_o solid at 130 K, slit 3.4 cm⁻¹, 1 × 10³ counts s⁻¹; (c) 1,4-dimethoxybenzene- d_o solid at 300 K, slit 3.2 cm⁻¹, 1 × 10³ counts s⁻¹; (d) 1,4-dimethoxybenzene- d_o , melt at 335 K, slit 3.4 cm⁻¹, 5 × 10² counts s⁻¹.

the CH₃ and CD₃ torsions. The torsional barriers, given in Table 1 are about the same as in anisole- a_0 and anisole- d_3 [27]. Upon deuteration the torsional barrier of the methyl group is reduced by 450 cm⁻¹, indicating a coupling between the methyl torsion and the out-of-plane bending ring mode. The coupling observed for 1,4-dimethoxybenzene is thus of the same order of magnitude as in the case of anisole.

The spectrum of liquid 1,4-dimethoxybenzene- cl_6 , Fig. 1(d), discloses an interesting new feature as compared to the spectrum of the solid, Fig. 1(c). A band absent in the solid state spectrum, appears at 359 cm⁻¹ in the spectrum of the melt. For the *trans* conformation the low-frequency C--X in-plane, in-phase vibration (derived from mode 15 according to Wilson's notation [33]) is a Raman forbidden transition. For the *cis* conformation this transition is allowed, since in this case it arises from a totally symmetric A_1 vibration. In the solid the molecules forming the crystal lattice exist exclusively in the *trans* conformation, whereas the proportion of *cis* conformers would be expected to rise with increasing temperature above the melting point. In addition, the allowed transition of the *cis* conformer should be polarized, which is indeed found to be the case for the 359 cm⁻² band. We therefore assign this band to the C--X in-plane, in-phase A_1 vibration of the *cis* conformer. The undeuterated compound behaves similarly,



Fig. 2. Expanded Raman spectra of the lattice region of 1,4-dimethozybenzene- d_{o} and 1,4-dimethoxybenzene- d_{o} , solid samples at 300 K: (a) 1,4-dimethoxybenzene- d_{o} , slit 3.2 cm⁻¹, 1 × 10⁴ counts s⁻¹; (b) 1,4-dimethoxybenzene- d_{o} , slit 3.2 cm⁻¹. \tilde{o} × 10³ counts s⁻¹.

but the new band in the spectrum of the melt appears at 370 cm⁻¹, partly overlapping the 380 cm⁻¹ band. To confirm the above tentative assignment, the temperature dependence of the 359 cm⁻¹ and 370 cm⁻¹ transitions should be investigated.

The spectra of the lattice region recorded are shown in Fig. 2, and the wavenumbers of the observed bands are listed in Table 2 together with the respective assignment. According to Goodwin and co-workers [28] 1,4-dimethoxybenzene crystallizes in the space group $P_{bca} = D_{2h}^{15}$ with four centrosymmetric molecules per unit cell. The four differently oriented molecules are located at sites having the symmetry of point group C_i . The correlation diagram which relates the factor group to the site group, and further to the point group C_{2h} of the isolated (rigid) molecule is shown in Table 3. The result of the factor group analysis is summarized in Table 4. It is seen that the lattice bands which are active in the Raman effect are of rotational type. Deuteration of the methocyl groups shifts all the bands in the lattice region to lower wavenumbers, but the largest shift is expected to be observed

TABLE 1

Assignment of torsional transitions (cm^{-1}) , and calculated barriers, V (cm^{-1}) , in 1,4-dimethozypenzene and its methyl deuterated analogue. Solid samples at 300 K if not otherwise indicated

Assignment	1,4-Dimethoxy	benzene-d _o	$1,4$ -Dimethoxybenzene- d_6		
	Transition	V	Transition	V	
Methyl torsion	264	1600	160	1150	
	265 ^E	1610	166 ^b	1230	
Methoxyl torsion	109	3220	99	3250	

^aSolid at 130 K, ^bMelt at 335 K.

TABLE 2

Observed transitions (cm⁻¹) in the lattice region of 1,4-dimethoxybenzene- d_{o} and 1,4-dimethoxybenzene- d_{o} together with their assignment. Solid samples at 300 K

1,4-Dimethoxybenzene- d_0	1,4-Dimethoxybenzene- $d_{_{ m G}}$	Assignment ^b		
41	38	Lattice $A_{\mathfrak{P}} B_{\mathfrak{1g}}$		
60	55	Lattice $A_{\mathfrak{P}} B_{\mathfrak{2g}}$		
84 [°]	82 ^e	Lattice $A_{\mathfrak{P}} B_{\mathfrak{2g}} B_{\mathfrak{1g}}$		
109	99	Methoxyl torsion		
115	113	Lattice $B_{\mathfrak{1g}} B_{\mathfrak{2g}}$		

⁴ Asymmetric band, consisting of several components. ⁵The assignment of the lattice transition to different representations is tentative and based on the calculation by Harada and Shimanouchi [41].

TABLE 3

Correlation diagram for the point group, site group and factor group of crystalline 1,4-dimethoxybenzene



for the methoxyl torsion. In the Raman effect only the in-phase B_g torsional mode is allowed. Careful examination of the high-frequency edge of the lattice region revealed a weak broad band, partly merged with the lattice transitions (Fig. 2). We thus obtain the transitions 199 cm⁻¹ for 1,4-di-

D _{2h}	⁷² tot	n _{ecoust}	r trensl	n _{rot}	n _{vib}	Activity	
						IR	Raman
 A_	30	0	0	3	27	_	$\alpha_{xz}, \alpha_{yy}, \alpha_{zz}$
B	30	C	0	3	27	_	2 _{V2}
B.2	30	0	0	3	27	_	azx
B	30	0	0	3	27		° _{xγ}
A.	30	0	3	0	27	—	_
B.,,	30	1	2	0	27	$T_{\mathbf{x}}$	-
B.,	30	1	2	0	27	T_{v}	<u> </u>
B_{3u}	30	1	2	0	27	T_z	_
Degrees of							
freedom	240	3	9	12	216		

Factor group analysis of crystalline 1,4-dimethoxybenzene, space group $P_{bce} = D_{2b}^{15}$; n = number of vibrations

methoxybenzene- d_0 and 99 cm⁻¹ for 1,4-dimethoxybenzene- d_6 , with the corresponding torsional barriers 3220 cm⁻¹ and 3250 cm⁻¹, or the same barrier height within the experimental error limits. The above assignment is in agreement with the work of Goulon et al. [23], who assumed that broad bands at 92 cm⁻¹ and 82 cm⁻¹ in the far IR spectrum of 1,4-dimethoxybenzene- d_0 and 1.4-dimethoxylenzene- d_6 in the solution arise from conributions of the IR-active out-of-phase torsional modes of both the cis and the trans conformers. Of the twelve Raman active lattice modes only four are observed in the present study. These bands (Table 2) correspond rather closely to those observed for crystalline benzene [34-40]. which seems reasonable, because benzene also crystallizes in the space group $P_{\rm bca}$ with four molecules per unit cell, and the lattice forces are the van der Waals type in both cases. The lattice bands of 1,4-dimethoxybenzene are rather broad, with a half-width of about 15 cm⁻¹. The band near 80 cm⁻¹ is clearly asymmetric, whereas the other lattice bands with the present resolution seem symmetric. However, the polycrystalline sample and relatively high sample temperature (130 K) used in the present study prevent a resolution of individual transitions. Ito et al. [40] studied the Raman spectra of benzene single crystals at 4.2 K and were able to resolve six of the twelve Raman active transitions. In addition they found that the width of Raman bands due to lattice vibrations decreases rapidly with decreasing temperature to about 1 cm⁻¹ at 4.2 K. Harada and Shimanouchi [41] calculated the lattice frequencies of benzene using a set of hydrogen-hydrogen force constants, and obtained excellent agreement with the experimentally observed bangs. They also reported the displacements of the hydrogen atoms for different Raman-active modes. In the present case, an unambiguous assign-

TABLE 4

ment of the lattice bands to different symmetry types would require oriented single crystal measurements, performed at lower temperatures than available with our present equipment.

CONCLUSIONS

The methyl and methoxyl torsional transitions have been identified in the low-frequency Raman spectrum of 1,4-dimethoxybenzene and the respective assignments have been confirmed with selective deuteration. The corresponding internal rotation barriers have been calculated according to the Mathieu model and compared with previous results for similar systems. Spectacular changes in the spectrum near 400 cm⁻¹, when going from solid to melt, have been interpreted as arising from the occurrence of both *cis* and *trans* conformations in the liquid state. A factor group analysis has been made indicating that all the Raman-active lattice modes are of rotational type. A tentative assignment of the lattice spectral region has been attempted for the first time in the present series of papers. In our earlier studies the explicit analysis of the lattice region was rendered impractical, because the crystal structure of the investigated compounds was unknown.

REFERENCES

- 1 H. Tylli, H. Konschin and C. Grundfelt-Forsius, J. Mol. Struct., 55 (1979) 157.
- 2 H. Konschin, H. Tylli and C. Grundfelt-Forsius, J. Mol. Struct., 77 (1981) 51.
- 3 H. Tylli, H. Konschin and C. Grundfelt-Forsius, J. Mol. Struct., 77 (1981) 37.
- 4 H. Konschin, H. Tylli and B. Westermark, J. Mol. Struct., 102 (1983) 279.
- 5 S. Mizushima, Y. Morino and H. Okazaki, Sci. Pap. List. Phys. Chem. Res. Tokyo, 34 (1938) 1147.
- 6 H. Hase, Z. Naturforsch., Teil A, 8 (1953) 695.
- 7 G. Klages, Z. Naturforsch., Teil A, 9 (1954) 366.
- 8 S. Mizushima, Structure of Molecules and Internal Rotation, Academic Fress, New York, 1954, pp. 90-92.
- 9 D. M. Roberti and C. P. Smyth, J. Am. Chem. Soc., 82 (1969) 2106.
- 10 M. Aroney, R. J. W. LeFevre and Shu-Sing Chang, J. Chem. Soc., (1960) 3173.
- 11 W. E. Vaughan and C. P. Smyth, J. Phys. Chem., 65 (1961) 98.
- 32 G. Klages and A. Zentek, Z. Naturforsch., Teil A, 16 (1961) 1016.
- 12 E. L. Grubb and C. P. Smyth, J. Am. Chem. Soc., 83 (1961) 4873.
- 14 W. L. Vaughan, S. B. W. Roeder and T. Provder, J. Chem. Phys., 39 (1963) 701.
- 15 E. Forest and C. P. Smyth, J. Am. Chem. Soc., 86 (1964) 3474.
- 16 D. B. Farmer, A. Holt and S. Walker, J. Chem. Phys., 44 (1966) 4116.
- 17 S. K. Garg and C. P. Smyth, J. Chem. Phys., 46 (1967) 373.
- 18 N. K. Mehrotra and M. C. Saxena, Indian J. Pure Appl. Fhys., 5 (1967) 1445.
- 19 D. B. Farmer and 2. Walker, Can. J. Chem., 47 (1969) 4645.
- 20 G. Klages and G. Kraus, Z. Naturforsch., Teil A, 26 (1971) 1272.
- 21 K. Chitoku, K. Higeshi, M. Nakaraura, Y. Koga and H. Taka Mashi, Bull. Chem. Soc. Jpn., 44 (1971) 992.
- 22 V. A. Granzan, S.F. Manole and S. K. Laktionova, Izv. Akad. Nauk Moid. SSR, Ser. Biol. Khim. Nauk, (1972) 72.
- 23 J. Goulon, D. Canet, M. Evans and G. J. Davies, Mol. Phys., 30 (1975) 973.
- 24 M. Marciq and J. S. Waugh, Chem. Phys. Lett., 47 (1977) 327.

- 25 E. T. Lippmaa, M. A. Alla, T. J. Pehk and G. Engelhardt, J. Am. Chem. Soc., 100 (1978) 1929.
- 26 M. M. Sushchinskii, Raman Spectra of Molecules and Crystals, Israel Program for Scientific Translations, New York, 1972, pp. 321-331.
- 27 H. Tylli and H. Konschin, J. Mol. Struct., 42 (1977) 7.
- 28 T. H. Goodwin, M. Przybylska and L. M. Robertson, Acta Crystallogr., 3 (1950) 279.
- 29 A. I. Kitzigorodskii, Organic Chemical Crystallography, Consultants Bureau, New York, 1961, pp. 357-358.
- 30 K. S. Pitzer and W. D. Gwinn, J. Chem. Phys., 10 (1942) 428.
- 31 E. Ernstbrunner, R. B. Girling, W. E. L. Grossman and R. E. Hester, J. Chem. Soc. Perkin Trans. 2, (1978) 177.
- 32 D. Marjit, P. K. Bishui and S. B. Banerjee, Indian J. Phys., 46 (1972) 457.
- 33 E. B. Wilson, Jr., Phys. Rev., 45 (1934) 703.
- 34 S. C. Sirkar, Indian J. Phys., 10 (1936) 189.
- 35 I. Ichishima, J. Chem. Soc. Jpn., 70 (1949) 391.
- 26 I. Ichishima and S. Mizushima, J. Chem. Phys., 18 (1950) 1686.
- 37 A. Fruhling, J. Chem. Phys., 18 (1950) 1119.
- 38 A. Fruhling, Ann. Phys. (Paris), 6 (1951) 401.
- 39 M. Ito, J. Chem. Phys., 42 (1965) 284 ±.
- 40 M. Ito and T. Shigeoka, Spectrochim. Acta, 22 (1966) 1029.
- 41 I. Harada and T. Shimanouchi, J. Chern. Phys., 44 (1966) 2016.