Free Radical Studies by Resonance Raman Spectroscopy. Part 1. The 1,4-Dimethoxybenzene Radical Cation

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The short-lived 1,4-dimethoxybenzene radical cation has been generated in acidic aqueous solution by oxidation of the parent molecule with cerium(IV). By performing the reaction under fast flow conditions the free radical has been studied in a steady-state condition by resonance Raman spectroscopy. Molecular orbital and normal co-ordinate calculations have been employed in analysing the resulting spectra in terms of the changes in structure and bonding which accompany radical formation in this system.

VIBRATIONAL spectroscopy has been used in a small way for free radical studies,[1] but generally has been found to lack the sensitivity and specificity required, particularly where the radical species of interest occur as transient intermediates in reacting systems. Resonance enhancement effects in Raman spectroscopy have been exploited in the present work to overcome some of the major difficulties in the way of vibrational analysis of the structures of transient free radicals.

It has been amply demonstrated that Raman band intensity enhancement factors of up to approx. 10^6 may result from exciting a Raman spectrum with incident radiation which is coincident in its wavelength with wavelengths associated with allowed electronic transitions of the species under study.[2] This great increase in sensitivity has been utilized in Raman studies of a wide variety of species, from simple inorganic to complex biological,[3,4] in solution (both aqueous and non-aqueous)

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[1] R. E. Hester, 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden and Son, London, 1977, vol. 4.

[2] J. Behringer, *Z. Elektrochem.*, 1957, **62**, 544.

[3] R. J. H. Clark, 'Advances in Infrared and Raman Spectroscopy,' eds. R. J. H. Clark and R. E. Hester, Heyden and Son, London, vol. 1, ch. 4, 1975; T. G. Spiro and T. M. Loehr, *ibid.*, ch. 3.

[4] E. Mayer and R. E. Hester, *J.C.S. Faraday II*, 1973, 1350.

at the 10^{-4}—10^{-5}M level of concentration. Since resonance enhancement is specific to the absorbing species (the free radicals of interest here), potential interferences from solvent and other polyatomic solute species may be virtually eliminated. Thus a free radical species at very low concentration can give rise to the strongest bands in a solution spectrum, even in the presence of a large excess of a parent compound and/or radical decay products and relatively high concentrations of other reagents, such as buffers, *etc.*

Several of the advantages claimed for the resonance Raman method already have been demonstrated in our earlier communication[5] concerned with the relatively stable *p*-phenylenediamine radical cation in methanol solution. By utilizing fast-flow methods derived from the e.s.r. field,[6] we have now extended the method to short-lived radicals. These may be observed in a steady-state condition at any point in a flow system downstream from the mixer unit. The focused laser beam which excites the Raman spectrum provides a much finer resolution (of distance along the flow stream and hence time after mixing) than is possible with e.s.r. equipment. By varying reactant concentrations, solution flow rates, and the length of the flow tube between mixer and observation cell, the profile of a chemical reaction may be monitored from times as short as a few milliseconds after mixing, upwards. The resonance Raman method is not subject to e.s.r.-type interferences, such as line broadening effects, and the method is equally applicable to non-radical species.

The paper describes the production, by means of oxidation in aqueous solution, of the 1,4-dimethoxybenzene (DMOB) radical cation, measurements of its Raman spectrum, and interpretation of the spectrum in terms of bond order and concomitant force constant changes with relation to the parent molecule. As a necessary preliminary, a normal co-ordinate analysis of the parent DMOB was also undertaken and is reported here.

TABLE 1

Kinetics of 1,4-dimethoxybenzene cation radical formation and decay from optical absorbance measurements

Concentrations					Decay
[DMOB]/mM	[Ce^{4+}]/mM	λ_{max}/nm	Al^{-1}/cm^{-1}	t_{max}/s	$t_{1/2}$/s
10 *	2	450	0.8	1.5	3
10	4	440	1.3	0.8	3.4
10	6	440	1.6	0.7	3.0
20	6	440	1.9	0.65	2.3
20	10	440	2.8	0.45	2.2
20 †	10	433	2.7	1.1	steady
		458	2.5	(flow rate 1.5 cm^3 s^{-1})	state

* Stopped flow. † Continuous flow. Pulse radiolysis gave λ_{max} 430 (ε 9 040 l mol^{-1} cm^{-1}) 460 (9 540) nm. Al^{-1} = absorbance per unit path length. t_{max} = time to reach maximum absorbance. $t_{1/2}$ = half-life of absorbing species.

RESULTS

DMOB in 20% acetone–0.5M-H_2SO_4 in water was mixed with Ce^{IV} in 0.5M-H_2SO_4. The formation and decay of the radical cation were observed, first under stopped flow, then under continuous flow conditions at various concentrations of both reagents, as shown in Table 1 and Figure 1(a). The absorption spectrum of the radical is shown in Figure 1(b)

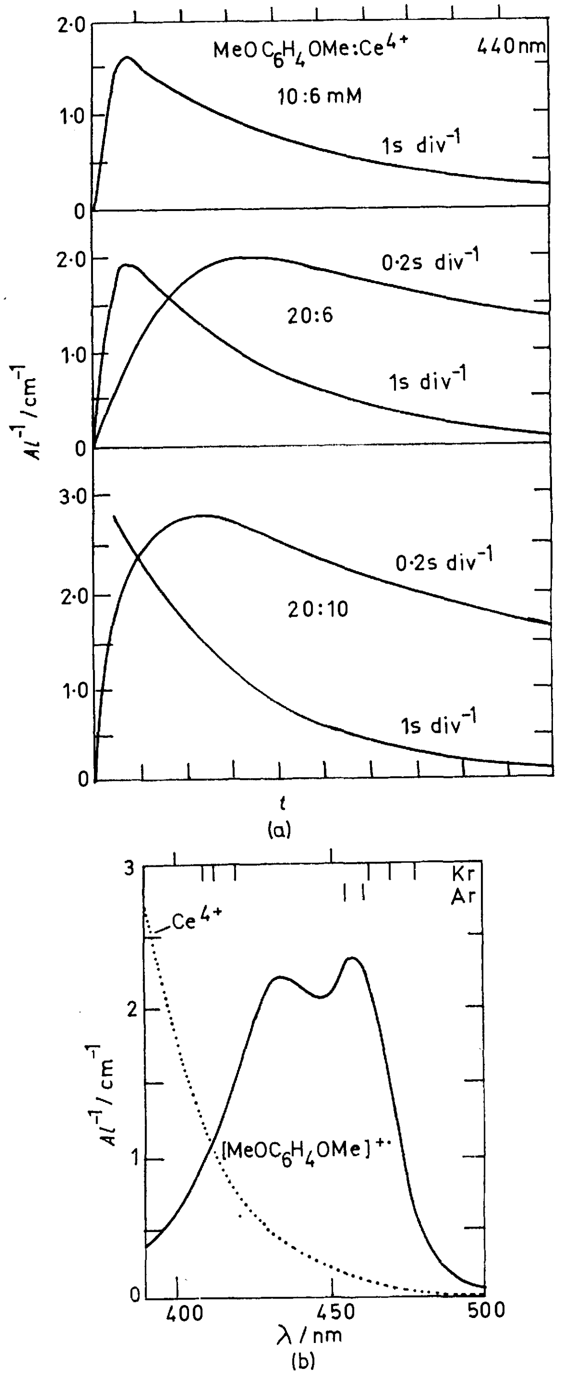

FIGURE 1 Kinetic and absorption data from the reaction between 1,4-dimethoxybenzene and cerium(IV) sulphate in 10% acetone–water with added 0.5M H_2SO_4: (a) stopped flow; (b) continuous flow corrected for Ce^{4+} absorption

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[5] E. Mayer, R. B. Girling, and R. E. Hester, *J.C.S. Chem. Comm.*, 1973, 192.

[6] R. O. C. Norman, 'Molecular Spectroscopy,' Institute of Petroleum, London, 1971; B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174, and other papers in this series.

and agrees with that published previously (obtained radiolytically [7]). The resonance Raman spectrum is seen in Figure 2, having been obtained from that of the original reacting mixture [trace (A)] by subtracting the spectra of the solution's other components, measured separately. Raman shifts and relative intensities are listed in Table 2; since all bands, with one possible exception, are polarized, they are to be assigned to totally symmetric vibrations only.

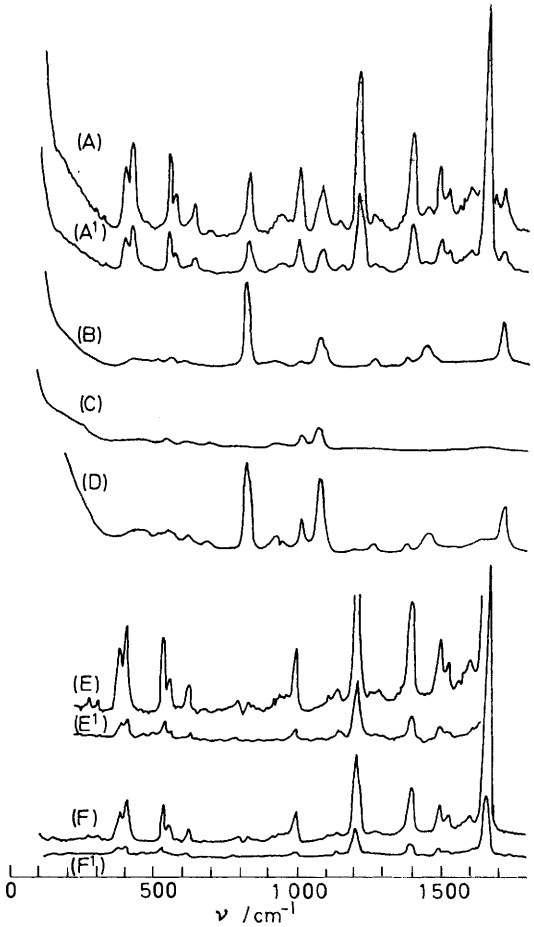


FIGURE 2 Raman spectra from (A) a reacting mixture of 1,4-dimethoxybenzene (7mM) and Ce^{IV} (7mM) in 10% acetone–water with added 0.5M-H_2SO_4; (B) 1,4-dimethoxybenzene (20mM) in 20% acetone–water with added 0.5M-H_2SO_4; and (C) $Ce(SO_4)_2$ (10mM) in 0.5M-H_2SO_4. Spectrum (D) = B) + 2(C), and (F) = (A)—(D), with scaling. Spectrum (E) = 2 × (F), and (A) = 2 × (A'). Spectra (E') and (F') were obtained with a perpendicular analyser, all others with parallel polarization. 476.2 nm excitation

DISCUSSION

Our main interest here is in the evaluation of structural and electronic changes upon radical formation, as manifested in the vibrational spectrum. It was therefore important to determine the principal force constants in the radicals studied. In the case of $DMOB^{+\cdot}$ this would not have been directly possible, with only some 11 totally symmetric fundamentals observed and no basis for an assignment. Comparison with the parent molecule was the only meaningful method. No previous normal co-ordinate analysis of DMOB existed, though the i.r. and Raman spectra had been measured.[8]

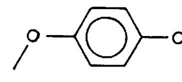
TABLE 2

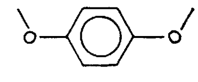
Raman spectrum of 1,4-dimethoxybenzene radical cation excited by 476.2 nm Kr laser line

ν/cm^{-1}	Relative intensities	Depolarization ratio
1 647	260	0.22
1 638	sh (220) *	p
1 584	8	~0.1
1 510	15	0.2
1 477	28	0.25
1 382	sh (28) *	p
1 375	30	0.25
1 278	8	0.3
1 198	sh (60) *	p
1 186	80	0.35
1 124	6	dp?
979	33	0.18
615	12	0.3
550	15	0.2
530	35	0.3
404	40	0.22
382	25	0.3

* By curve-resolving.

Normal Co-ordinate Analysis.—DMOB is known to be planar, both in the solid state [9] and in solution.[10] In the crystal the *trans*-form (A) (C_{2h}) obtains, while solutions contain a roughly equal mixture of (A) and the *cis*-form (B) (C_{2v}).[10] The effect of this conformational change on the vibrational spectrum is small, according to trial calculations, except for low frequencies. Since the spectra obey the mutual exclusion rule,[8] and since in the radical the *trans*-form predominates,[7] we assumed C_{2h} symmetry. Bond lengths and angles were taken from the crystal data.[9] The x-axis was chosen perpendicular to the ring.


(A)


(B)

Under C_{2h} symmetry the 54 vibrations can be divided into 30 ring modes ($11a_g + 5a_u + 4b_g + 10b_u$) and 24 substituent modes ($7a_g + 5a_u + 5b_g + 7b_u$). The CH_3 torsions ($a_u + b_g$), observed [10] at 92 cm^{-1}, were neglected. The remaining observed frequencies are shown in Table 3, with tentative assignments (for the ring modes we follow Wilson's notation [11]). With few exceptions, our assignment agrees with the previous one.[8] The band at 373 cm^{-1}, however, could not be fitted to an a_g mode within a reasonable force field; we ascribe it to an a_1 mode of the *cis*-conformer (B) (calculated at 366 cm^{-1}

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[7] P. O'Neill, S. Steenken, and D. Schulte-Frohlinde, *J. Phys. Chem.*, 1975, **79**, 2773.

[8] D. Marjit, P. R. Bishui, and S. B. Banerjee, *Indian J. Phys.*, 1972, **46**, 457.

[9] J. H. Goodwin, M. Przybylska, and J. M. Robertson, *Acta Cryst.*, 1950, **3**, 279.

[10] J. Goulon, D. Canet, M. Evans, and G. J. Davies, *Mol. Phys.*, 1975, **30**, 973.

[11] E. B. Wilson, *Phys. Rev.*, 1934, **45**, 706.

using the refined force field transferred from the *trans*-form). The 550 and 520 cm^{-1} Raman bands if assigned to a_u modes[8] would both be forbidden; the latter we found to correspond with a strong i.r. band at 517 cm^{-1} (solid and CCl$_4$ solution). We therefore assign the a_u mode to 517 cm^{-1}, the 550 cm^{-1} band to the missing a_g fundamental, and the Raman-active 520 cm^{-1} mode to the latter's counterpart in the *cis*-conformer (B) (calculated at 539 cm^{-1}). These assignments are corroborated by the spectrum of the radical which shows similar splittings. Finally, we observed and assigned three more i.r. active vibrations (472, 419, and 246 cm^{-1}).

TABLE 3

Observed and calculated vibrational spectrum of 1,4-dimethoxybenzene

	ν/cm^{-1}				
	Obs.[a]	Calc.	Difference	Assignment[d]	P.e.d.[e]
a_g	3 071[b]	3 050.3		ar. ν(CH)	100 S_1
	3 048[b]	3 045.7		ar. ν(CH)	100 S_2
	3 002	3 002.0	0.0	as. $\nu(CH_3)$	94 S_{12}
	2 836/2 939[c]	2 851.7		symm $\nu(CH_3)$	95 S_{13}
	1 610	1 610.0	0.0	8a	38 S_3, 33 S_5
	1 588	1 588.0	0.0	8b	72 S_4
	1 462	1 461.7	0.3	as. $\delta(CH_3)$	90 S_{15}
	1 452	1 452.1	−0.1	symm $\delta(CH_3)$	72 S_{16}
	1 307	1 307.0	0.0	7a (X sens)	33 S_3, 47 S_6
	1 264	1 264.0	0.0	3 [β(CH)]	98 S_7
	1 180	1 180.1	−0.1	9a [β(CH)]	97 S_8
		1 142.5		$\rho(CH_3)$	81 S_{17}
	1 030	1 030.6	−0.6	O–CH$_3$ stretch	71 S_{14}, 23 S_{16}
	820	820.0	0.0	1 (X sens)	49 S_5, 26 S_6
	635	635.0	0.0	6b	49 S_9, 21 S_{18}
	550	550.0	0.0	9b (X sens)	85 S_{11}
	406	406.0	0.0	6a	52 S_{10}
		191.5		Skeletal	26 S_9, 70 S_{18}
b_u	3 040[b]	3 052.5		ar. ν(CH)	100 S_{19}
	3 027[b]	3 051.2		ar. ν(CH)	100 S_{20}
	3 002	3 002.0	0.0	as. $\nu(CH_3)$	94 S_{29}
	2 836/2 939[c]	2 851.4		symm $\nu(CH_3)$	95 S_{30}
	1 515	1 515.0	0.0	19a	21 S_{22}, 35 S_{24}
		1 463.1		19b	31 S_{23}, 20 S_{32}
	1 462	1 462.1	−0.1	as. $\delta(CH_3)$	77 S_{32}
	1 420	1 420.1	−0.1	symm $\delta(CH_3)$	56 S_{33}
	1 292	1 292.0	0.0	14	72 S_{21}, 28 S_{23}
	1 240	1 240.0	0.0	13 (X sens)	20 S_{24}, 59 S_{25}
	1 150	1 150.0	0.0	$\rho(CH_3)$	70 S_{34}
	1 104	1 104.0	0.0	15 [β(CH)]	24 S_{23}, 73 S_{26}
	1 042	1 042.2	−0.2	18a [β(CH)]	31 S_{22}, 45 S_{28}
	1 019	1 018.5	0.5	O–CH$_3$ stretch	74 S_{31}, 23 S_{33}
	709	709.0	0.0	12 (X sens)	41 S_{24}, 23 S_{28}
	472	472.0	0.0	18b	27 S_{27}, 38 S_{35}
		157.7		Skeletal	41 S_{27}, 49 S_{35}
b_g	2 946	2 946.0	0.0	as. $\nu(CH_3)$	99 S_{36}
	1 462	1 462.0	0.0	as. $\delta(CH_3)$	99 S_{37}
	1 178	1 178.0	0.0	$\rho(CH_3)$	94 S_{38}
	845	845.0	0.0	10a [γ(CH)]	59 S_{40}, 32 S_{41}
	798	798.0	0.0	5 [γ(CH)]	100 S_{39}
	710	710.0	0.0	4	32 S_{40}, 61 S_{41}
	279	278.7	0.3	10b (X sens)	44 S_{41}, 39 S_{42}
		140.1		$\tau(OCH_3)$	43 S_{41}, 40 S_{42}
a_u	2 946	2 946.0	0.0	as. $\nu(CH_3)$	99 S_{44}
	1 462	1 461.8	0.2	as. $\delta(CH_3)$	99 S_{45}
	1 178	1 178.1	−0.1	$\rho(CH_3)$	94 S_{46}
	937	937.0	0.0	17a [γ(CH)]	91 S_{48}
	827	826.9	0.1	11	73 S_{47}
	517	517.1	−0.1	16a	90 S_{49}
	419	418.9	0.1	17b (X sens)	45 S_{50}, 52 S_{51}
	246	246.0	0.0	16b	65 S_{50}, 35 S_{52}
		91.8		$\tau(OCH_3)$	28 S_{51}, 58 S_{52}

[a] Ref. 8 and present measurements. [b] Not used in refinement (see text). [c] Fermi resonance (see text). [d] Wilson's classification of aromatic vibrations.[11] [e] Potential energy distribution (%) among symmetry co-ordinates.

Of the remaining 46 observed fundamentals, the four aromatic ν(CH) vibrations were not used in the force field refinement, because of the usual uncertainty in assignment. The symmetric CH$_3$ stretching modes are subject to Fermi resonance[12,13] and were not assigned to a definite frequency.

Wilson's GF method, as embodied in the Snyder–

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[12] P. Labarbe and M. J. Forel, *Spectrochim. Acta*, 1968, **24A**, 2165.

[13] D. C. McKean, *Chem. Comm.*, 1971, 1373.

TABLE 4

Symmetry co-ordinates (not normalized) of dimethoxybenzene (internal co-ordinates shown in Figure 3 *)

a_g

$S_1 = s_2 + s_3 + s_5 + s_6$
$S_2 = s_2 - s_3 + s_5 - s_6$
$S_3 = t_2 + t_5$
$S_4 = t_1 - t_3 + t_4 - t_6$
$S_5 = t_1 + t_3 + t_4 + t_6$
$S_6 = s_1 + s_4$
$S_7 = \phi_3 - \phi_4 + \phi_5 - \phi_6 + \phi_9 - \phi_{10} + \phi_{11} - \phi_{12}$
$S_8 = \phi_3 - \phi_4 - \phi_5 + \phi_6 + \phi_9 - \phi_{10} - \phi_{11} + \phi_{12}$
$S_9 = \phi_1 - \phi_2 + \phi_7 - \phi_8$
$S_{10} = 4\alpha_1 - 2\alpha_2 - 2\alpha_3 + 4\alpha_4 - 2\alpha_5 - 2\alpha_6 - 2\phi_1 - 2\phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 - 2\phi_7 - 2\phi_8 + \phi_9 + \phi_{10} + \phi_{11} + \phi_{12}$
$S_{11} = 2\alpha_2 - 2\alpha_3 + 2\alpha_5 - 2\alpha_6 - \phi_3 - \phi_4 + \phi_5 + \phi_6 - \phi_9 - \phi_{10} + \phi_{11} + \phi_{12}$
$S_{12} =$ as. $\nu(CH_3)$
$S_{13} =$ symm $\nu(CH_3)$
$S_{14} = p_1 + p_2$
$S_{15} =$ as. $\delta(CH_3)$
$S_{16} =$ symm $\delta(CH_3)$
$S_{17} = \rho(CH_3)$
$S_{18} = \psi_1 + \psi_2$

b_u

$S_{19} = s_2 + s_3 - s_5 - s_6$
$S_{20} = s_2 - s_3 - s_5 + s_6$
$S_{21} = t_2 - t_5$
$S_{22} = t_1 - t_3 - t_4 + t_6$
$S_{23} = t_1 + t_3 - t_4 - t_6$
$S_{24} = s_1 - s_4$
$S_{25} = \phi_3 - \phi_4 + \phi_5 - \phi_6 - \phi_9 + \phi_{10} - \phi_{11} + \phi_{12}$
$S_{26} = \phi_3 - \phi_4 - \phi_5 + \phi_6 - \phi_9 + \phi_{10} + \phi_{11} - \phi_{12}$
$S_{27} = \phi_1 - \phi_2 - \phi_7 + \phi_8$
$S_{28} = 2\alpha_1 - 2\alpha_2 + 2\alpha_3 - 2\alpha_4 - \phi_1 - \phi_2 + \phi_3 + \phi_4 - \phi_5 - \phi_6 + \phi_7 + \phi_8 - \phi_9 - \phi_{10} + \phi_{11} + \phi_{12}$
$S_{29} =$ as. $\nu(CH_3)$
$S_{30} =$ symm $\nu(CH_3)$
$S_{31} = p_1 - p_2$
$S_{32} =$ as. $\delta(CH_3)$
$S_{33} =$ symm $\delta(CH_3)$
$S_{34} = \rho(CH_3)$
$S_{35} = \psi_1 - \psi_2$

b_g

$S_{36} =$ as. $\nu(CH_3)$
$S_{37} =$ as. $\delta(CH_3)$
$S_{38} = \rho(CH_3)$
$S_{39} = \gamma_2 + \gamma_3 - \gamma_5 - \gamma_6$
$S_{40} = \gamma_2 - \gamma_3 - \gamma_5 + \gamma_6$
$S_{41} = \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$
$S_{42} = \gamma_1 - \gamma_4$
$S_{43} = \tau_7 + \tau_8$

a_u

$S_{44} =$ as. $\nu(CH_3)$
$S_{45} =$ as. $\delta(CH_3)$
$S_{46} = \rho(CH_3)$
$S_{47} = \gamma_2 + \gamma_3 + \gamma_5 + \gamma_6$
$S_{48} = \gamma_2 - \gamma_3 + \gamma_5 - \gamma_6$
$S_{49} = \tau_1 - 2\tau_2 + \tau_3 + \tau_4 - 2\tau_5 + \tau_6$
$S_{50} = \tau_1 - \tau_3 + \tau_4 - \tau_6$
$S_{51} = \gamma_1 + \gamma_4$
$S_{52} = \tau_7 - \tau_8$

* τ_1 to τ_6 represent out-of-plane CCCC torsional co-ordinates corresponding to bonds t_1 to t_6; γ_1 to γ_6 represent the out-of-plane co-ordinates corresponding to bonds s_1 to s_6.

Schachtschneider programs,[14] was used in our calculations. Our internal and symmetry co-ordinates, based on Scherer,[15] are shown in Figure 3 and Table 4. The G matrix elements were calculated through GMAT (with the bond angle deformations not scaled). An initial force field, composed of Scherer's data for the aromatic vibrations[15] and of the force constants of dimethyl ether,[12] totalling some 50 parameters, was drawn up. Using a refinement procedure similar to Shimanouchi's[16] that, in addition, allowed us to introduce various forms of constraint we were able, by introducing a few additional force constants, to fit all the observed frequencies to within 1 cm^{-1} [Table 3, which also lists an abbreviated potential energy distribution (p.e.d.)]. The final 55 parameters and their values are shown in Figure 4.

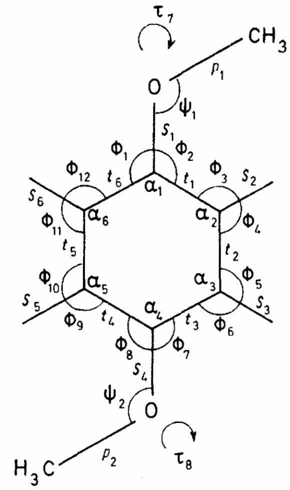

FIGURE 3 Internal co-ordinates of 1,4-dimethoxybenzene

In the absence of isotopic data the problem was somewhat underdetermined, though many of the aromatic diagonal and interaction force constants would not be expected to differ much from their values in other compounds. Therefore, and in view of our subsequent analysis of the radical cation whose vibrational spectrum is much less complete, we introduced constraints on the C–O and C–C stretching force constants. These are known to be related to π-bond orders[17] which we calculated by the INDO method[18] (Figure 5A). Within the small range found a linear relationship $\Delta F_{rs} = a_{rs}\,\Delta p_{rs}$ can be assumed; from the generally accepted force constants for single and double C–C and C–O bonds we deduce a_{CC} 4.5, a_{CO} 8.0. Thus, $F_{1\text{-}7} - F_{7\text{-}8} = 0.49$ and $F_{2\text{-}3} - F_{2\text{-}1} = 0.161$. (Very similar increments of 0.37 and 0.13 are calculated by combining relationships between

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[14] J. M. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, 1963, **19**, 117.

[15] J. R. Scherer, *Spectrochim. Acta*, 1964, **20**, 345; 1967, **23A**, 1489.

[16] T. Shimanouchi, 'Computer Programs for Normal Coordinate Treatment of Polyatomic Molecules,' Tokyo, 1968.

[17] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, 1939, **35**, 811.

[18] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

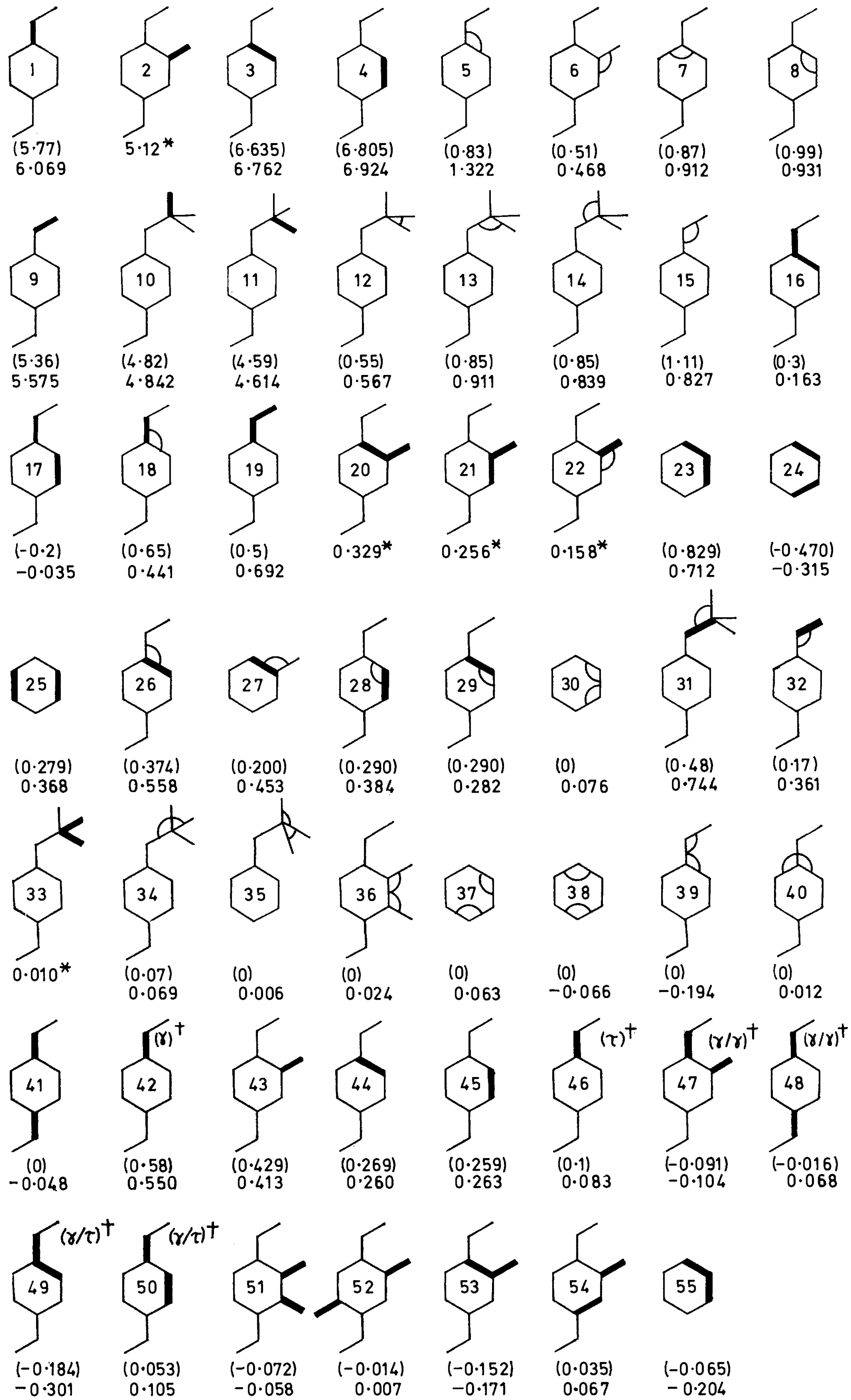

FIGURE 4 In-plane (1—41) and out-of-plane (42—55) force constants (mdyn Å^{-1}, mdyn Å rad^{-2}, mdyn rad^{-1}). * Not included in refinement procedure. † Otherwise ambiguous; γ denotes out of plane, τ denotes torsion

bond lengths and PPP bond orders [19,20] on the one hand and bond lengths and force constants [21] on the other, illustrating, incidentally, the caution necessary in employing bond lengths alone; $r = r_{12} - r_{23}$ is calculated as 0.54 pm, but was measured as 30 pm; [9] a more recent study of diethoxybenzene [22] indicates -0.5 ± 1.0 pm). As Figure 4 shows, most of the final force constants are quite close to the originally assumed values.

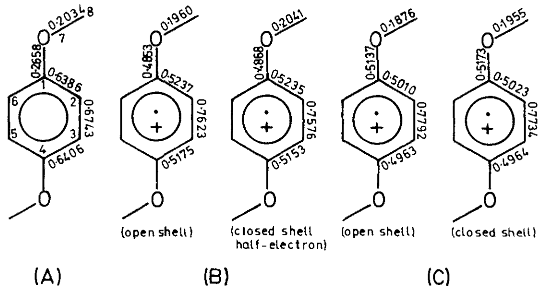

FIGURE 5 INDO π-bond orders of 1,4-dimethoxybenzene (A) and its radical cation; original (B) and adjusted (C) geometry

An estimate of the changes in the force field on converting DMOB into the radical cation is now possible with the help of MO calculations. In Figures 5B and 5C are shown the π bond orders in the radical, computed in the INDO approximation, both by the UHF method [18] (' open shell ') and by the half-electron method.[23] The differences between the two sets are small. If these are compared with the bond orders in the parent molecule (Figure 5A), the intuitively expected ' quinonoid ' structure of the radical emerges quite clearly. The MO calculations can be tested by comparing experimental [7] and calculated ^{1}H hyperfine coupling constants from e.s.r. spectra. These are listed in Table 6 and show moderate agreement; as in the case of *p*-benzosemiquinone, the aromatic hyperfine coupling constants are too low.[24] Slightly better results are obtained by the half-electron method or by adjusting the molecular geometry, but most of the discrepancy is probably due to solvent effects.[25]

TABLE 5

Comparison of observed and calculated Raman frequencies (cm^{-1}) for 1,4-dimethoxybenze and its cation radical, and their assignments

DMOB Obs./calc.*	Assignment	DMOB$^{+\cdot}$ Obs.	DMOB$^{+\cdot}$ Calc.
1 610	ring (8a)	1 647	1 656
1 607 †		1 638 ‡	1 655
1 588	ring (8b)	1 584 §	1 527
		1 510 §	
1 462	as. δ(CH_3)	1 477	1 474
1 452	symm δ(CH_3)		1 463
1 307	X-sens (7a)	1 382 ‡	1 397
1 300/1 306 †		1 375	1 390
1 264	β(CH) (3)	1 278	1 263
1 180	β(CH) (9a)	1 186	1 181
1 180/1 180 †		1 198 ‡	1 180
1 150	ρ(CH_3)	1 124?	1 144
1 030	O–CH_3 stretch	979	1 022
820	X-sens (1)		825
635	ring def. (6b)	615	633
550	X-sens (9b)	550	548
520/539 †		530 ‡	539
406	ring def. (6a)	404	413
373/366 †		382 ‡	370

* Identical for *trans*-conformer. † Calculated for *cis*-conformer with identical force field. ‡ *cis*-Conformer (see text). § Fermi resonance (see text).

TABLE 6

Observed [8] and calculated e.s.r. hyperfine coupling constants (^{1}H) for the 1,4-dimethoxybenzene cation radical

		Original geometry		Adjusted geometry	
	Obs.	Open shell	Half-electron	Open shell	Half-electron
CH_3	3.41	4.43 *	3.52 *	3.68 *	2.88 *
H_1	1.59	(−) 0.94	1.34 †	(−) 1.03 †	1.50 †
H_2	2.92	(+) 1.38	1.63 †	(−) 1.38 †	1.75 †

* Averaged over all three protons. † *via* McConnell relation (H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, *J. Amer. Chem. Soc.*, 1960, **82**, 766).

The linear relationship between force constants and bond orders now allows us to estimate the stretching force constants in the radical; these, together with the original ones in DMOB, are shown in Figure 6. We finally chose the average values of 6C; actually the choice does not affect final frequencies by more than a few cm^{-1}. As changes in bending force constants are not directly predictable, and as spectral changes in the low frequency region are much less dramatic (Table 5) we did not alter them, nor was the G matrix adjusted for the slightly different geometry of the radical. The new force field then produces the calculated frequencies listed in Table 5. The agreement with the bands observed for the radical is quite reasonable and allows direct assignments. The shoulders on some bands (1 647, 1 375, 1 186 cm^{-1}) can be ascribed to the presence of the *cis*-conformer; resolution of these doublets by

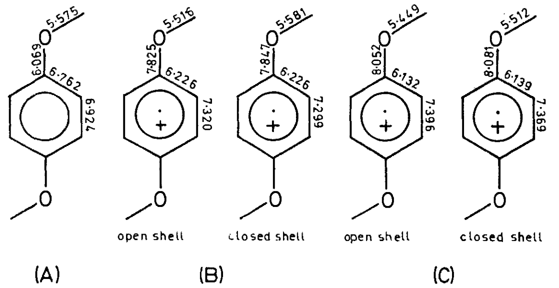

FIGURE 6 Stretching force constants of 1,4-dimethoxybenzene (A) and its radical cation; original (B) and adjusted (C) geometry

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[19] O. Gropen and P. N. Skancke, *Acta Chem. Scand.*, 1970, **24**, 1768.

[20] G. Höjer, *Acta Chem. Scand.*, 1969, **23**, 2589.

[21] K. J. Bernstein and S. Sunder, Proc. 5th Internat. Conf. Raman Spectrosc., 1976, p. 153.

[22] M. Haisa and S. Kashino, *Acta Cryst.*, 1977, **B33**, 485.

[23] M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 1968, **90**, 1953.

[24] Ref. 18, p. 148.

[25] J. Spanget-Larsen, *Chem. Phys. Letters*, 1976, **44**, 543.

computer shows intensity ratios of $(1.1 \pm 0.3):1$, compared with a conformer ratio, as determined by e.s.r., of 1.12.[7] Similarly, the doublets 550/530 and 404/382 cm^{-1} can be assigned to the mixture of *cis*- and *trans*-forms [corroborating our assignment of the 520 and 373 cm^{-1} bands in the parent to the *cis*-form (B)]. The two bands 1 584 and 1 510 cm^{-1} cannot both be fundamentals; we ascribe the former to Fermi resonance of (1 186 + 404) or (979 + 615) with both 1 647 and 1 510 cm^{-1}; this would mean an unperturbed value for the latter of *ca.* 1 530 cm^{-1}, based on intensity, compared to the calculated 1 534 cm^{-1}. The largest discrepancy is found between the observed band at 979 cm^{-1} and the calculated 1 022 cm^{-1}, which is insensitive to stretching force constant changes. Because of the low number of known frequencies in the radical, force field refinement is impractical; it may be significant, however, that all the remaining differences between observed and calculated frequencies above 900 cm^{-1} can only be accounted for by adjusting some of the OCH_3 force constants.

Conclusions.—The Raman spectrum of the unstable 1,4-dimethoxybenzene cation radical in aqueous solution has been found to differ substantially from that of its parent molecule. After determining the previously unknown force field of the parent we have been able, with the help of semi-empirical MO calculations, to evaluate changes in stretching force constants accompanying radical formation. The corresponding frequency predictions agree well with the observed spectrum. The free radical spectrum showed more polarized bands than predicted, but this was accounted for by the presence of a second conformer, previously detected by e.s.r. measurements; our ratio of concentrations (assuming equal cross-section for both conformers) agrees with the earlier estimate, and the splitting observed in some bands is well reproduced by our force field (identical for both conformers). Thus the utility of the resonance Raman method has been established for both structural and analytical studies of free radicals in solution.

EXPERIMENTAL

1,4-Dimethoxybenzene and cerium(IV) sulphate (' low in other rare earths ') were B.D.H. Laboratory Reagent grade, used without further purification. Solutions were made up with distilled water and purged with nitrogen. Reactions were carried out by an e.s.r.-type continuous flow arrangement: each solution was held in a 5 dm^3 reservoir with gravity feed, from which they passed through flow meters to a mixing chamber and then a 0.1×10 mm cross-section sample cell. Raman spectra were recorded by an instrument consisting of a Jobin–Yvon HG2 Ramanor monochromator, a RCA C31034A/02 photomultiplier, Brookdeal 9511 quantum photometer, and a Nicolet 1074 signal averager and PDP 11 minicomputer linked to a DEC 10 computer for accumulating and processing spectra. Excitation was by Spectra Physics 170 krypton laser. Band intensities were measured on an arbitrary scale as relative peak heights and depolarization ratios were determined with the aid of a polarizer in the scattered light beam, followed by a polarization scrambler placed in front of the monochromator entrance slit.

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