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Vibrational spectra, scaled quantum-mechanical (SQM) force field and assignments for 4H-pyran-4-one

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Abstract—The gas phase i.r. spectrum of 4H-pyran-4-one (hereafter called γ-pyrone) has been recorded in the 4000–400 cm^{-1} region by a Nicolet 7199 FTIR spectrometer and interpreted using a general valence force field calculated quantum mechanically at the *ab initio* level with a split-valence 4-21 basis. Assignment of certain fundamentals was facilitated by information gained from the i.r. and Raman spectra of the melt and from the i.r. spectrum of the saturated solution in CCl_4.

To account for systematic computational errors, the theoretical *ab initio* force field was scaled using a set of constants derived by the empirical fitting of force fields computed for related molecules to their observed spectra. Either the scale factors derived for a family of open-chain molecules or, better, for benzene could be used to yield a scaled force field which gave unequivocal assignments for γ-pyrone. The method promises to be of general applicability for molecules of this complexity.

INTRODUCTION

Harmonic force fields of polyatomic molecules play an essential role in the interpretation of vibrational spectra and in the prediction of other vibrational properties. It is well established now (see, e.g., Ref. [1]) that fully empirical force fields suffer from major deficiencies in this respect, largely because complete force fields cannot be determined from experimental data for molecules containing more than a very few atoms without the use of large numbers of unsubstantiated assumptions.

On the other hand, purely theoretical calculations at levels of quantum-mechanical sophistication adequate to be of use in distinguishing between possible near-by frequencies for assignment to a given fundamental vibration cannot be done except for very simple molecules. For such purposes it would be desirable to be able to determine harmonic force constants with an accuracy of at least 2%, corresponding to an error of 1% in the associated vibrational frequencies. Useful improvement beyond this level would require a more advanced treatment than the usual isolated harmonic oscillator approximation. Computation of a force field even at this level, however, requires a large basis set *ab initio* calculation with a good treatment of electron correlation so that it is impractical for medium-sized molecules.

Recent experience has shown a way to resolve the dilemma. It has been shown to be possible to compute a complete harmonic force field at a modest *ab initio* level within the SCF approximation for a known molecule, optimize a small number of scale factors to fit the spectrum which this force field produces to the known spectrum, and then transfer those scale factors to correct the computed force field of a related molecule. The resulting force field, called a scaled quantum mechanical (SQM) force field [1], does not make use of any experimental information from the molecule under investigation, but it is not strictly an *ab initio* force field since it does involve the transfer of experimental information from a known related molecule. It has been called an *a priori* determination to emphasize that no spectral information need be known about the molecule under study. The transfer of scale constants constitutes an assumption that the *error* in computing a given type of force constant, as well as the effect of anharmonicity, is similar in related molecules. This assumption is obviously better as the error becomes smaller, so that *ab initio* force fields of resonable accuracy (double zeta or better) are best suited to the method, although useful results have been obtained even with semi-empirical levels of calculation. For reviews, see Refs. [1–5].

In one major test of the transferability of scale factors, the force field of benzene was calculated *ab initio* at the Hartree–Fock level using a Gaussian 4-21 basis set [6]. This force field was then scaled using either six or nine adjustable scale factors to give the best fit to the observed spectra of benzene and some of its deuterated isotopomers [7]. Next, the in-plane [8] and out-of-plane [9] force fields of pyridine were calculated at the same level of quantum chemical approximation. These force fields were then scaled with the scale factors that had been optimized for

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benzene, the spectra of pyridine and its isotopomers computed, and the predicted frequencies and intensities compared with the observed spectra. The same experiment of transferring the benzene scale factors has been performed with computed force fields of naphthalene [10] and aniline [11]. Comparison between *a priori* prediction and experiment has uniformly shown agreement within the harmonic oscillator approximation limits in these cases. For example, the mean deviation between the observed and predicted spectra of naphthalene was only 6.5 cm^{-1}.

Similar tests of the transferability of scale factors have been made for a variety of other molecules including cubane [12], triprismane [13], imidazole [14], pyrrole [15], maleimide [16] and uracil [17]. In all of these studies, the spectra which were predicted *a priori* by the transfer of scale factors from related molecules were compared with already existing spectral data, so in no case until now have computed scaled quantum mechanical force field predictions been used simultaneously with the experimental determination of the vibrational spectra to obtain direct interpretation of the experimental results. We report here the first such study, making use of the SQM spectral predictions to assign newly made measurements on the i.r. and Raman spectra of γ-pyrone.

No detailed gas-phase vibrational spectra have been reported previously for γ-pyrone. Earlier studies of its i.r. spectrum [18–23], that of its salts [22], and of its protonated forms [23], mainly in $CHCl_3$ and CCl_4 solutions, found that Fermi resonance occurs between the first overtone of the very intense C–H out-of-plane and the carbonyl stretching vibrations [18, 21]. Accordingly, the exact position of the pure carbonyl stretching mode has not yet been assigned unambiguously. A detailed but not fully complete analysis of the i.r. spectra of γ-pyrone was reported by KATRITZKY and JONES [19] and KATRITZKY and TAYLOR [20]. From far i.r. measurements in the gas phase, the frequencies of the two lowest i.r.-active out-of-plane ring torsional modes were given by SMITHSON *et al.* [24] as 424 and 149 cm^{-1}. The lower frequency determined in this way is in acceptable agreement with the value of 123 cm^{-1} calculated from the microwave spectrum by MACDONALD *et al.* [25]. A normal coordinate analysis of γ-pyrone has also been reported by PIETRZYSKI [26]. In this work, a Urey–Bradley force field was used and only the in-plane vibrations were considered. Unfortunately, we cannot reproduce the spectral frequencies used by PIETRZYSKI in this analysis.

EXPERIMENTAL

γ-Pyrone was prepared by decarboxylation of chelidonic acid [27] following the procedure given in the experimental part of Ref. [25]. The purity of the samples used for taking the spectra was checked using a VG-7035 GC–MS system.

The gas-phase i.r. spectrum of γ-pyrone was taken in the region of 4000–400 cm^{-1} using a Nicolet 7199 FTIR spectrometer. The sample was held in a commercial Zeiss cell equipped with KBr windows at a temperature of 35 ± 1°C. The cell, with a fixed path length of 1 m, was evacuated prior to introduction of the sample, so the pressure within the cell was to a very good approximation equal to the saturated vapor pressure of γ-pyrone at 35°C. A resolution of 0.12 cm^{-1} was achieved by using 131 072 data points and 262 144 transformation points. An apodization function of type BX was used, and the number of scans was 1260. For recording the spectra, a M.C.T. detector cooled with liquid nitrogen was used.

The Raman spectrum of the γ-pyrone melt was recorded with a Jobin-Yvone Ramanor HG-2S spectrometer in the region of 3200–2900 and 2000–120 cm^{-1}. The sample was redistilled prior to use and placed in a Pyrex capillary held at 37 ± 0.5°C. The incident light was the 514.5 nm line of a Zeiss-made Ar^+ ion laser with a nominal output of 10 mW. The incident light was linearly polarized, enabling the determination of the depolarization ratios, which have a maximum value of 3/4 at the perpendicular arrangement of the detector we have used.

The i.r. spectrum of the γ-pyrone melt was taken with a PE-283B spectrophotometer using normal slit programming for the region 3200–400 cm^{-1}. The sample was held at 55 ± 0.5°C in a commercial KBr liquid cell.

To facilitate unambiguous assignment of the gas-phase i.r. spectra, certain regions of the spectrum were also taken of the saturated CCl_4 solution with the Nicolet FTIR spectrometer.

The overview gas-phase i.r. spectrum and the Raman spectrum of the melt are given in Figs 1 and 2, respectively.

COMPUTATIONAL DETAILS

The SQM force field of γ-pyrone was calculated using methods that have been previously described [1, 2]. If scale factors are to be transferred from related molecules, it is important that the true equilibrium geometry be used as the point around which the potential energy is expanded to obtain the harmonic force field elements. It has been pointed out [1] that the best approximation to this geometry is often obtained by the use of the empirically corrected computed geometry [6] because of vibrational averaging commonly remaining in experimentally determined structures. In the case of γ-pyrone, however, there has been an unusually extensive microwave structural study leading to a complete substitution (r_s) structure for the molecule. While there is no fixed relation between r_s and r_e structures, it is commonly believed that the difference is small except for heavy atom–hydrogen distances. Furthermore, in our particular case we would need the offset value for an ether C–O bond to correct a theoretical structure, and this value is quite uncertain [28]. Accordingly, we have adopted the experimental substitution structure [25] for our reference structure, correcting the C–H bond lengths to 107.9 and 107.6 pm for α and β CH bonds, respectively.

Energy gradients were calculated using the program TEXAS [29]. Second derivatives of the energy (the force field elements) were obtained numerically by systematic displacements along the internal coordinates shown in Table 1 and Fig. 3. The changes applied were 2 pm for bond stretching motions, 0.028 rad for in-plane and out-of-plane exo-ring bendings, and 0.049 rad for in-plane bendings and torsions of the ring, with the exception of q_2 and τ''_{ring} for which

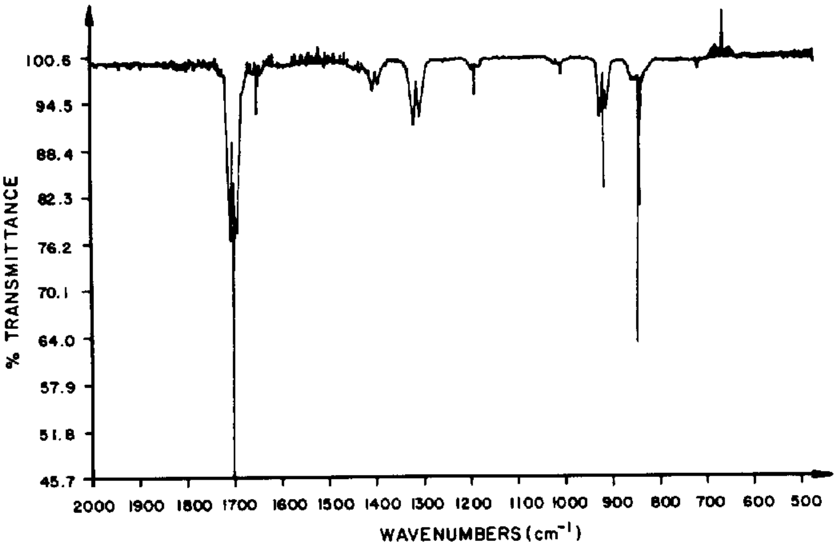


Fig. 1. Gas phase i.r. spectrum of γ-pyrone in the region of 2000–450 cm^{-1}.

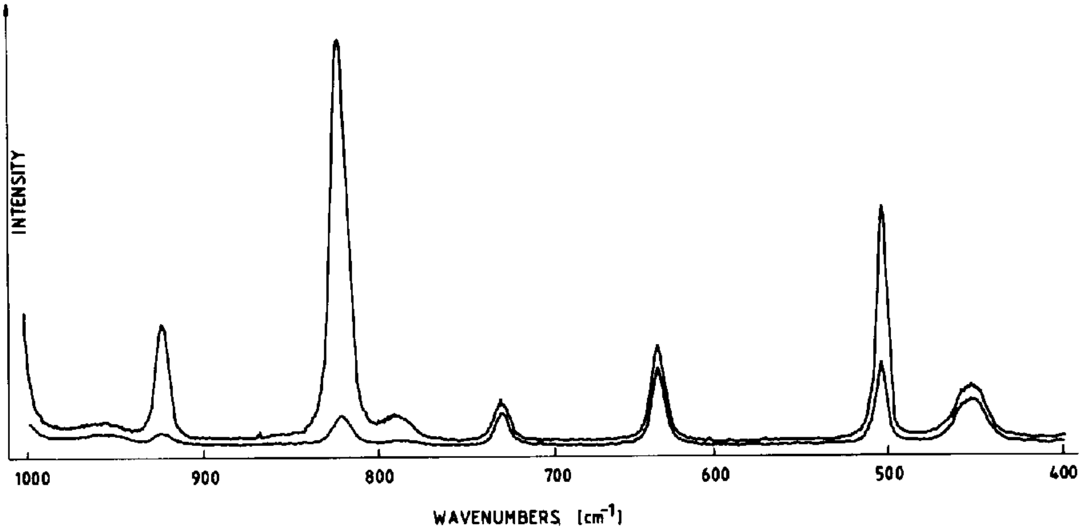


Fig. 2. Raman spectrum of the melt γ-pyrone in the region of 1000–400 cm^{-1}.

Table 1. Internal coordinates for γ-pyrone

No.	Coordinate*	Notation	Description
1, . . . , 5	$r_1 \ldots r_5$	$\nu_{CH}, \nu_{C=O}$	C–H and C=O str.
6, . . . , 11	$R_1 \ldots R_6$	$\nu_{C-C}, \nu_{C=C}, \nu_{CO}$	C–C, C=C and C–O str.
12, . . . , 16	$\beta_1 = \phi_1 - \phi'_1; \ldots \beta_5 = \phi_5 - \phi'_5$	$\beta_{CH}, \beta_{C=O}$	C–H and C=O bend.
17, . . . , 19	$q_1 = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$	β'_{ring}	Ring deformation
	$q_2 = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	β''_{ring}	Ring deformation
	$q_3 = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	β'''_{ring}	Ring deformation
20, . . . , 24	$\delta_1, \ldots \delta_5$	$\delta_{CH}, \delta_{C=O}$	C–H and C=O out-of-plane bend.
25, . . . , 27	$t_1 = \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$	τ'_{ring}	Ring torsion
	$t_2 = 2\tau_2 - \tau_1 - \tau_3 + 2\tau_5 - \tau_4 - \tau_6$	τ''_{ring}	Ring torsion
	$t_3 = \tau_1 - \tau_3 + \tau_4 - \tau_6$	τ'''_{ring}	Ring torsion

*For notation see Fig. 3. Normalization factors are omitted. The out-of-plane bending coordinates are positive if atom $i+6$ moves in the negative y direction.

τ_i denotes the torsion around the bond between atoms i and $i+1$; it is positive when, viewing from the direction of $i+1$, an anti-clockwise rotation is needed to bring atoms $i+2$ and $i-1$ into eclipsed conformation.

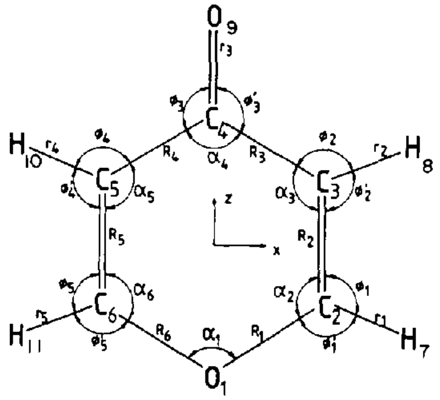


Fig. 3. Notation for geometric parameters and internal coordinates of γ-pyrone.

displacements of 0.04 rad were used. Both positive and negative displacements were made so that the effect of cubic anharmonicity could be minimized [1], except for those motions having no cubic terms by symmetry. In all calculations, the split-valence 4-21 basis [6] was used.

To obtain the SQM force field, the theoretical force constants were scaled as described in Ref. [1]. The scaling was carried out in three alternative ways, the first two of which involved transfer of scale factors from other molecules and therefore yield *a priori* prediction of the spectrum. Calculation I used the scale factors derived in Ref. [1] by the simultaneous fitting of a number of open-chain molecules. In calculation II, the scale factors derived for benzene [7] were used. There is little difference between the two sets of scale factors, but it might be assumed that the factors derived for the six-membered ring would be more closely related to γ-pyrone. On the other hand, benzene has no direct analog for the C–O and C=O linkages for which scale factors had to be assumed as described below. Finally, once the experiment and the theoretical predictions had led to a confident assignment of the fundamental frequencies, calculation III derived a refined set of scale factors for γ-pyrone by least-squares fitting of the calculated frequencies to the experimental ones. Off-diagonal force constants smaller than 0.005 were omitted when optimizing the scale factors, and only the unambiguously assigned gas-phase frequencies were taken into account. Calculation III does not give an independent prediction of the frequencies, of course, but it does provide useful information in assessing the constancy of scale factors in a variety of molecules.

Terms derived from the M-matrix were used for characterization of the forms of the normal modes [30–32]. The M_{ij} element of this matrix is proportional to the weight of the jth internal coordinate in the ith normal mode.

To estimate the absolute i.r. band intensities, the dipole moment derivatives with respect to the internal coordinates have also been calculated [6, 30–32]. According to experience with the split-valence 4-21 basis set [2–5], the intensity data obtained in this manner are qualitatively correct, thus facilitating the assignment of the fundamentals.

RESULTS AND DISCUSSION

Vibrational spectra and assignments

The experimental and calculated vibrational frequencies obtained from the SQM force field of γ-pyrone are given in Table 2 together with other information available on the intensities, band shapes and the depolarization of the Raman lines.

For interpretation of the spectra, we accepted the result from the microwave study [25] that the molecule is planar and possesses C_{2v} symmetry. The 27 normal modes are distributed among the irreducible representations in the following way:

$$\Gamma = 10a_1 + 3a_2 + 9b_1 + 5b_2.$$

The normal modes of a_2 symmetry are i.r.-inactive but Raman-active; the remaining ones are both i.r.- and Raman-active. Enumeration of the fundamentals follows the conventional order of the symmetry species given in textbooks of group theory.

The i.r.-active modes of a_1, b_1 and b_2 symmetry have A, B and C type band contours with P–R separations of 14, 9 and 14 cm^{-1}, respectively. The Raman lines are all depolarized except those of a_1 symmetry.

One can observe that theoretical frequencies obtained using either the scale factors transferred from open-chain molecules (calculation I) or the set transferred from benzene (calculation II) are in fairly good agreement with the experiments. Relatively large differences, as large as 20–40 cm^{-1}, can only be found in the region of the double-bond stretchings, i.e. between 1800 and 1600 cm^{-1}. It is claimed [18–21] that this region of the spectra taken in solution is strongly affected by Fermi resonances, an effect not accounted for in the theoretical harmonic treatment. Accordingly, this region of the spectrum was handled with special care, as discussed below.

The individual assignments are discussed below, first the in-plane modes, then the out-of-plane ones. Emphasis is placed on the gas-phase i.r. spectrum, and other experimental results are considered to the extent that they help in the interpretation of the gas-phase spectra or identify the a_2 i.r.-inactive fundamentals. In a very large number of cases, the computed results were of great value in selecting between alternative assignments. This theoretical assistance has enabled us to make a complete assignment without resorting to experimental study of isotopically substituted species.

In-plane vibrations

C–H *stretching region* (3200–2900 cm^{-1}). On the basis of structural evidence (symmetry) and the *a priori* computed results (calculations I and II), one can predict the appearance of two well-separated bands in this region of the i.r. spectrum. The band with higher

Table 2. Experimental and calculated frequencies of γ-pyrone

Experimental frequencies*					Calculated frequencies†			
CCl$_4$Sol. i.r.	Melt i.r.	Melt Raman	Gas i.r.	Assignments	I	II	III	I$_{abs}$‡
	3125 sh	**3130** w, P		$\nu_1(a_1)$	3106	3106	3101	0.08
	3095 sh	3095 w, D	**3098** vw, *B*	$\nu_{14}(b_1)$	3103	3103	3098	0.53
	3076 w	**3076** w, P		$\nu_2(a_1)$	3073	3072	3072	0.03
	3030 sh	3025 vw, P		$\nu_{15}(b_1)$	3072	3072	3067	0.04
	2965 vw	2950 vw, D						
	2880 vw							
2785 vw	2775 vw							
	2725 vw							
2630 vw	2630 vw							
2595 vw	2585 vw							
2430 vw	2430 vw							
2235 vw	2240 vw							
2045 vw	2050 vw							
1945 vw	1950 vw							
1890 vw								
1855 vw	1860 vw							
1820 vw	1835 vw							
1820 vw	1835 vw							
1795 vw	1780 vw							
1733 vw	1743 vw	1740 vw, ?						
			1702 vs, *A*	$\nu_3(a_1)$	1678	1707	1715	24.49
1695 w	1700 sh	1700 w, P	1699 vw, *A*	$\nu_6+\nu_{10}(A_1)$				
			1687 vw, *A*	$2\nu_{24}(A_1)$				
1676 vs	1673 vs	1672 m, D						
1656 s	1659 vs	1658 vs, P	**1652** m, *A*	$\nu_4(a_1)$	1607	1649	1642	12.47
	1638 s	1633 s, P						
1621 m								
1600 sh	1607 s	**1610** s, D		$\nu_{16}(b_1)$	1559	1611	1590	0.30
1570 vw	1560 sh	1563 m, D						
	1535 vw	1535 sh, D						
1455 w	1465 w	1460?	1443 w, *B*	$\nu_9+\nu_{21}(B_1)$				
			1412 w, *B*	?				
1405 m	1414 m	1415 sh, D?	**1401** m, *B*	$\nu_{17}(b_1)$	1406	1416	1405	19.01
1385 sh	1395 sh	1398 w, P?		$\nu_5(a_1)$	1380	1373	1382	0.05
1340 vw								
1312 vs	1317 s	1318 w, D	**1314** s, *B*	$\nu_{18}(b_1)$	1317	1316	1322	6.27
1265 vw	1272 vw							
	1260 vw		1255 vw, *B*	$\nu_{13}+\nu_{24}(B_1)$				
1216 w	1217 w	1220 sh, D		$\nu_{19}(b_1)$	1220	1220	1217	0.003
1195 m	1197 m	1198 m, D	**1193** m, *A*	$\nu_6(a_1)$	1197	1194	1201	0.06
1115 vw	1122 vw	1122 vw, D						
			1034 vw, *B*					
1023 w	1026 w	1029 m, D	**1019** w, *B*	$\nu_{20}(b_1)$	1013	1024	1020	0.96
1010 w	1009 m	1008 vs, P	**1010** w, *A*	$\nu_7(a_1)$	1006	1010	1011	0.001
960 vw	965 vw	**960** b, D						
				$\nu_{11}(a_2)$	965	965	976	—
				$\nu_{23}(b_2)$	959	964	970	0.26
922 vs	922 vs	924 m, P	**920** vs, *A*	$\nu_8(a_1)$	898	915	908	15.09
850 vs	850 vs	850 vw, D	**847** vs. *C*	$\nu_{24}(b_2)$	844	844	848	12.08
825 w	825 sh	822 vs, P		$\nu_9(a_1)$	849	811	803	0.05
812 w								
		790 w, P		$\nu_{12}(a_2)$	789	786	793	—
726 w	728 vw	730 m, D	**720** w, *C*	$\nu_{25}(b_2)$	723	716	714	0.05
625 vw	642 vw	641 m, D		$\nu_{21}(b_1)$	636	639	637	0.08
502 vw	503 vw	504 s, P		$\nu_{10}(a_1)$	490	493	494	0.07
458 m	450 m	453 b, D		$\nu_{22}(b_1)$	441	456	434	1.57
438 m			**424**	$\nu_{26}(b_2)$	434	430	429	0.30
407 w		**395** vw, D		$\nu_{13}(a_2)$	408	401	398	—
		(175 vw, ?)	**149** §	$\nu_{27}(b_2)$	158	156	155	0.14

*Frequencies are in cm^{-1}. The relative intensities of i.r. and Raman bands are denoted by vw = very weak, w = weak, m = medium, s = strong, vs = very strong, b = broad. P and D stand for polarized and depolarized Raman lines, respectively. *A*, *B* and *C* are the types of band contours in the gas phase i.r. spectrum. a_1, a_2, b_1 and b_2 are the symmetry of the fundamentals; A_1, A_2, B_1 and B_2 denote that of the overtones and combination bands.

†The frequencies in columns I, II, and III are obtained from calculations I, II, and III, respectively. See text for details.

‡Absolute intensities calculated from dipole moment derivatives with respect to the internal coordinates, in units of cm/mmol.

§Data taken from Ref. [16].

frequency (3098 cm^{-1}) and weak intensity belongs primarily to the asymmetric C–H stretching, ν_{14} (b_1), whose frequency essentially coincides with that of $\nu_1(a_1)$ which, according to the theoretical results, should be of much lower intensity. Support for this conclusion comes from the Raman spectrum of the melt in which a depolarized weak line is observed at 3095 cm^{-1} (see Fig. 4b) whose properties are characteristic of a normal mode of b_1 symmetry.

The melt also shows two polarized bands in the Raman spectrum. These are of higher intensity than the depolarized band, which is in accordance with the common observation that symmetric C–H Raman bands are of high intensity. The lower one of the polarized pair is at approximately the expected frequency shift below the b_1 band, and presumbaly corresponds to $\nu_2(a_1)$. The other band at 3130 cm^{-1} in the melt must be $\nu_1(a_1)$. Its unexpectedly high frequency may reflect condensed-phase interactions in the melt, a Fermi resonance interaction, or simply inaccuracy in the *ab initio* predicted frequency differences. The other b_2 band, ν_{15}, is not seen in the Raman spectrum of the melt. It is probably under one of the other peaks, most likely the one at 3076 cm^{-1}.

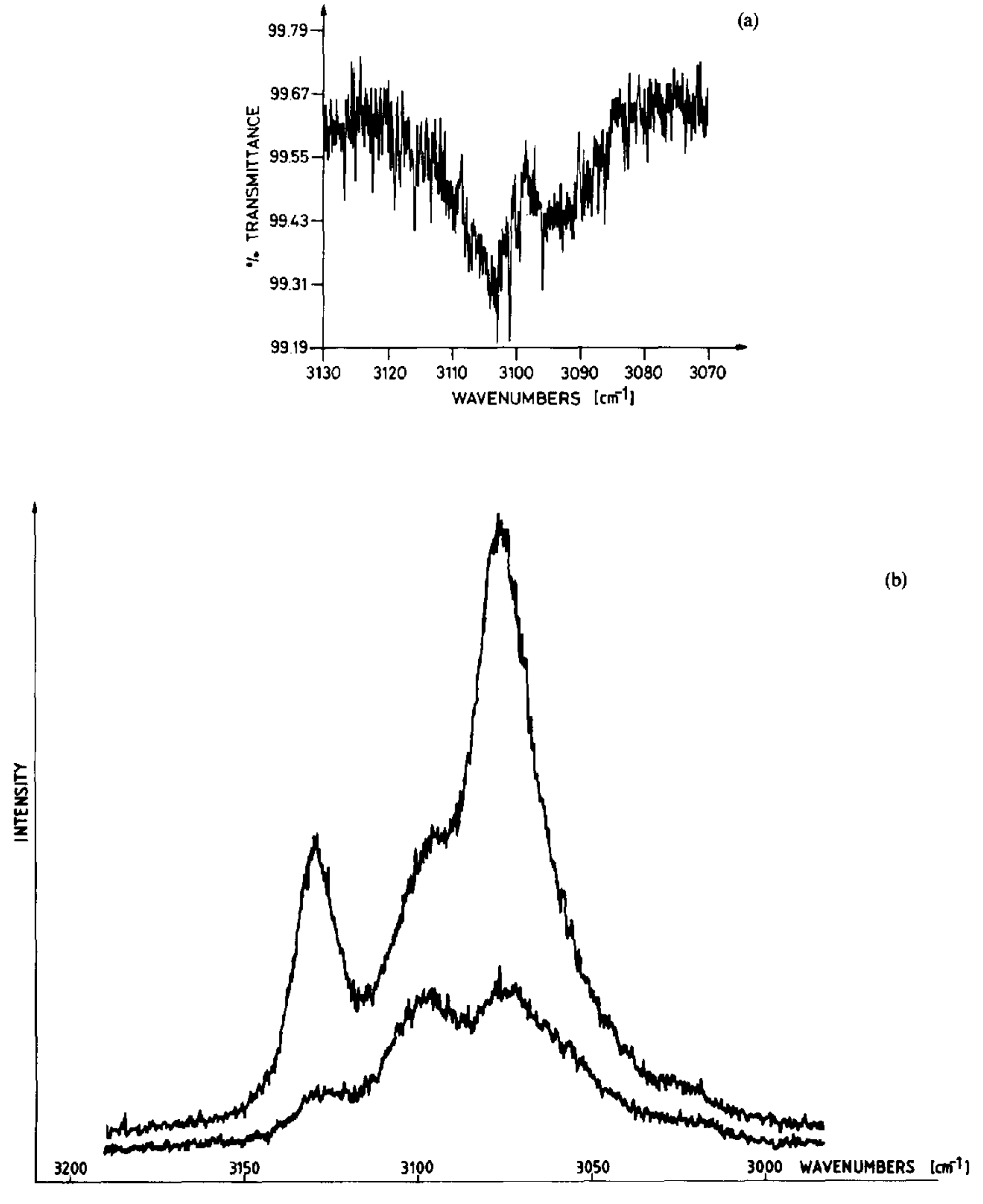


Fig. 4. Gas-phase i.r. (a) and liquid-phase Raman (b) spectra of γ-pyrone in the ν_{CH} region.

The $\nu_{C=O}$ and $\nu_{C=C}$ region (1800–1600 cm^{-1}). As mentioned above, it has been suggested [18, 21] that this region of the spectrum is complicated by Fermi resonances. In the light of our results, this is presumbably true only for spectra taken in condensed phases, since from the spectra shown in Fig. 5 it is seen that Fermi resonance apparently does not take place in the gas phase. The gas-phase i.r. spectrum is considerably simpler than that in melt or in solution. The number of observed bands is compatible with the number of normal modes and the form of the bands does not resemble Fermi doublets.

In the gas phase there are two characteristic A-type bands observed at 1702 and 1652 cm^{-1} which can be assigned to ν_3 (a_1) and $\nu_4(a_1)$, the pure C=O stretching and the symmetric C=C stretching, respectively. The third normal mode, the asymmetric C=C, $\nu_{16}(b_1)$, is predicted to be of low intensity and, for this reason, was not detected in the gas-phase spectrum, although we made considerable effort to do so. This unobserved fundamental also cannot be assigned with certainty from the spectra of condensed phases due to the complications from resonance observed there. It may be that the band at 1610 cm^{-1} observed in both i.r. and Raman spectra of the melt can be assigned to this band.

The region of C–H *bendings and single bond stretchings* (1500–1000 cm^{-1}). The observed bands in this region of the spectra are shown in Figs 6 and 7. The band at highest frequency, 1401 cm^{-1}, is ascribed to the normal mode $\nu_{17}(b_1)$ composed of C–O and C–C stretchings.

The most characteristic in-plane C–H bendings modes are the fundamentals $\nu_6(a_1)$ and $\nu_{18}(b_1)$ as shown in Fig. 7. The normal modes $\nu_5(a_1)$ and $\nu_{19}(b_1)$ are predicted to be of extremely low intensity and are not observed in the gas-phase spectra. The frequency of 1385 cm^{-1} assigned to $\nu_5(a_1)$ in the tables is taken from the spectrum of the saturated CCl$_4$ solution. On

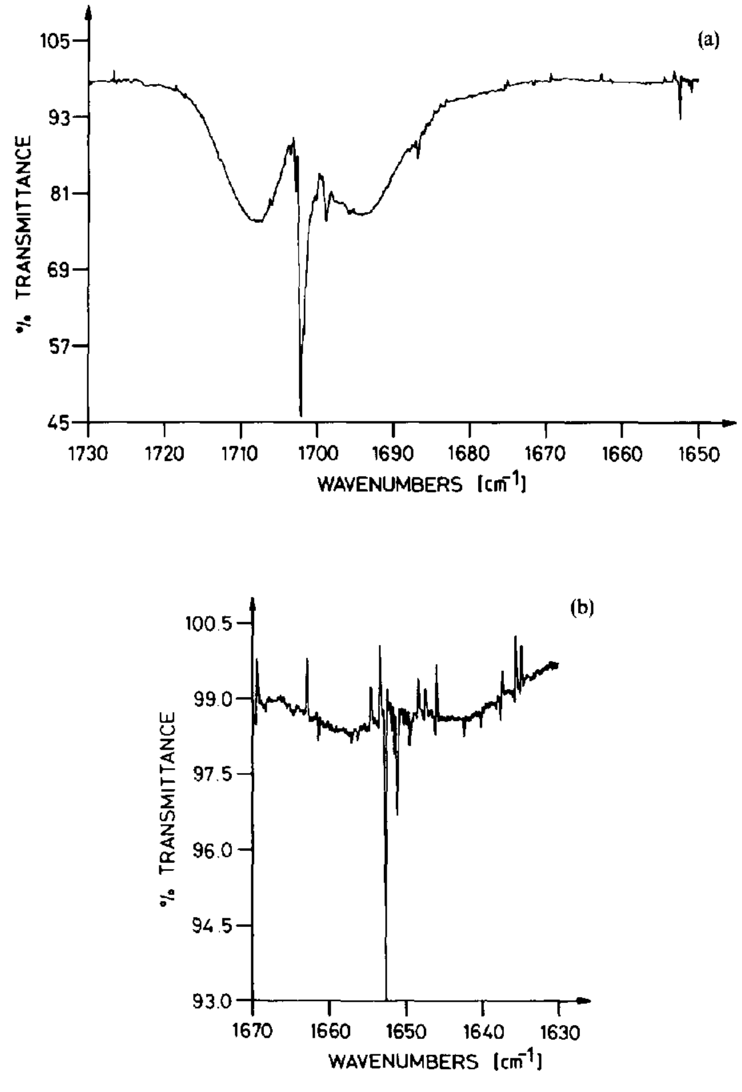


Fig. 5. (a and b).

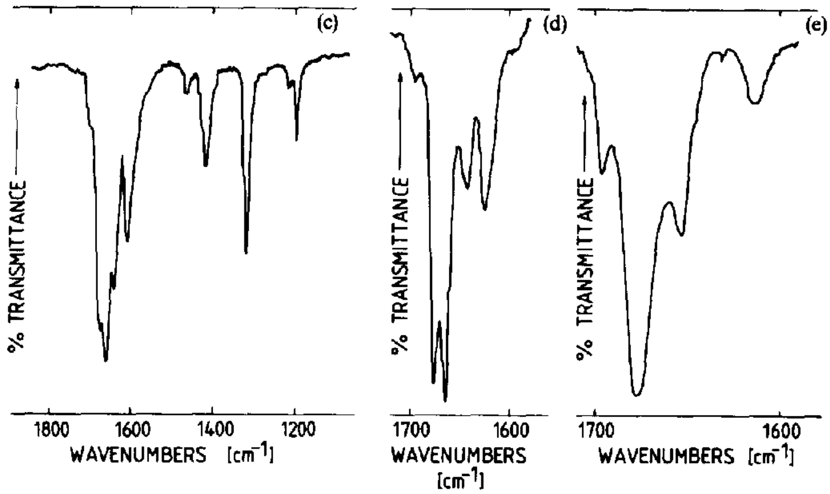


Fig. 5. Infrared spectrum of γ-pyrone in the double band stretching region. (a) The $\nu_{C=O}$ band, $\nu_3(a_1)$, in the gas-phase spectrum; (b) the $\nu_{s\,C=C}$ band, $\nu_4(a_1)$, in the gas-phase spectrum; (c) the spectrum of the melt; (d) the spectrum of the saturated $CHCl_3$ solution; (e) the spectrum of the saturated CCl_4 solution.

the basis of the *ab initio* predictions, the weak band at 1255 cm^{-1} (Fig. 8) was not taken as fundamental but has been assigned to a combination $\nu_{13}(a_2)+\nu_{24}(b_2)$. The band around 1216 cm^{-1} in the CCl_4 solution was ascribed to $\nu_{19}(b_1)$, a combination of the β_{CH} and $\beta_{C=O}$ bending modes. The remaining two bands at 1019 cm^{-1} and 1010 cm^{-1} (Fig. 9) are assigned to $\nu_{20}(b_1)$ and $\nu_7(a_1)$, the combinations of C–H bending with C–O stretching and in-plane ring bending, respectively.

In-plane vibrations below 1000 cm^{-1}. The *A*-type band observed at 920 cm^{-1} is shown in Fig. 10. It has been assigned to $\nu_8(a_1)$, the normal mode mainly consisting of β_{CH} mixed with the in-plane ring bending, q_1.

In accordance with the *ab initio* predictions, the next in-plane fundamental should be around 805 cm^{-1}, but with very low intensity. Accordingly, this band was not seen in the gas-phase spectrum. We have assigned the very weak band at 825 cm^{-1} observed in the i.r. spectra of the melt and the solutions to this fundamental, $\nu_9(a_1)$, a mode mainly of C–C stretch character. It is somewhat surprising that this band was not reported in earlier studies mentioned above.

The remaining fundamental of a_1 symmetry is predicted to lie at 490 cm^{-1}, but again it is of very low intensity and was not observed in the gas-phase i.r. spectrum. We assign the strong, polarized line at 504 cm^{-1} in the Raman spectrum of the melt to this fundamental, $\nu_{10}(a_1)$, consisting mainly of the ring in-plane deformation, q_2.

To complete the assignments of the in-plane vib-

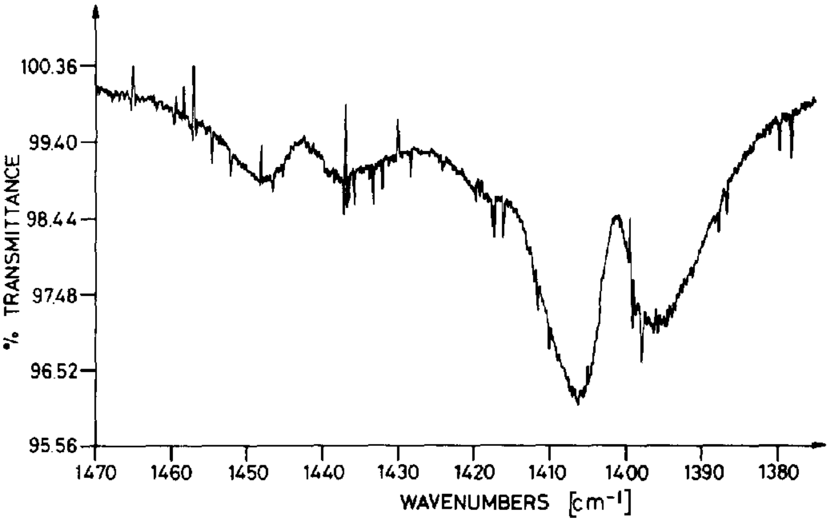
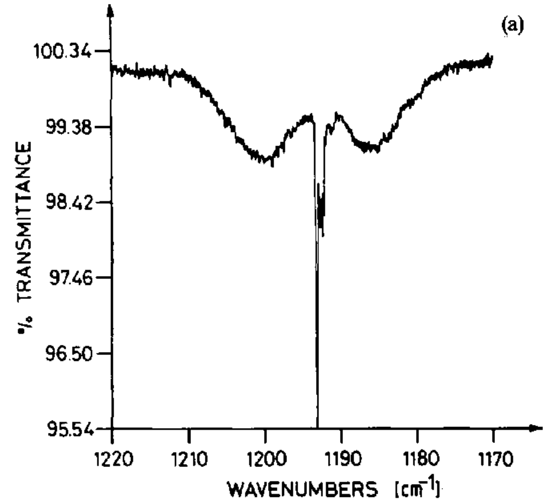


Fig. 6. The $\nu_{17}(b_1)$ band of γ-pyrone in the gas-phase i.r. spectrum at 1401 cm^{-1}.



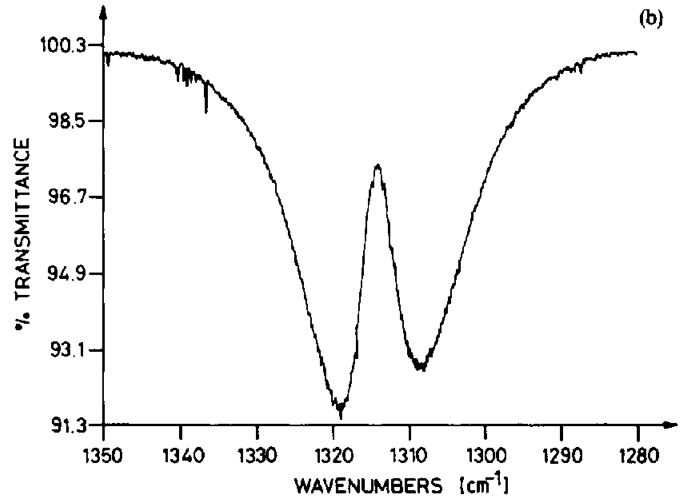


Fig. 7. The $\nu_6(a_1)$ and $\nu_{18}(b_1)$ bands of γ-pyrone in the gas-phase i.r. spectrum at 1193 cm^{-1} (a) and 1314 cm^{-1} (b), respectively.

rations, there remain two fundamentals of b_1 symmetry. The $\nu_{21}(b_1)$ and $\nu_{22}(b_1)$ fundamentals have *ab initio* predicted frequencies of 636 and 441 cm^{-1}, respectively. Due to their low intensity, they are not observed in the gas-phase spectra but were assigned to the depolarized lines at 641 and 453 cm^{-1}, respectively, in the Raman spectrum of the melt.

Out-of-plane vibrations

Out-of-plane fundamentals are sometimes disregarded in experimental vibrational studies with the argument that the respective bands are of low intensity, hardly observable and do not consistitute the essential part of the vibrational spectra. One extreme opinion is that out-of-plane vibrations "are not of much importance to forming of the spectra as a whole" [26]. This opinion is hardly acceptable because these normal modes can be of very high intensity, contributing much to the overall picture of the spectra.

In this respect, one of the most encouraging features of the method employed by us, i.e. the prediction of vibrational frequencies and intensities from SQM force fields, is that there is no distinction between in-plane and out-of-plane modes of a planar molecule; the latter can be as easily predicted as the former. Even frequencies for inactive modes can be calculated with useful accuracy, although one should be very cautious when describing unobserved fundamentals and the suggested assignments should be regarded as tentative until some experimental evidence provides confirmation.

In the out-of-plane spectrum of γ-pyrone, there are three a_2 and five b_2 normal modes, only three of which are observed in the gas-phase spectrum recorded by us.

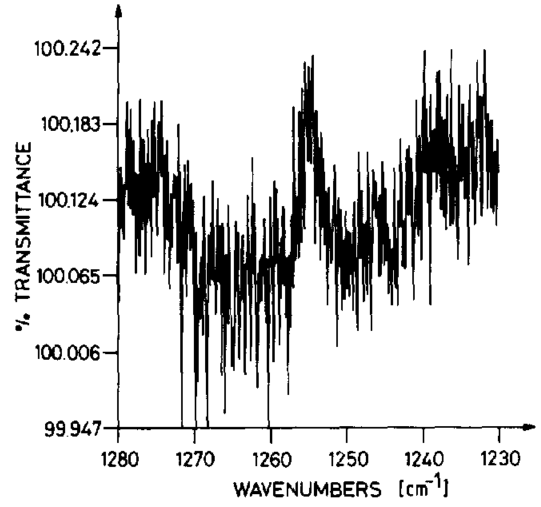


Fig. 8. The hardly detectable B-type band at 1255 cm^{-1} in the gas-phase i.r. spectrum of γ-pyrone.

The missing frequencies are connected with the out-of-plane motions of the C–H bonds and with the low-frequency ring torsions. Experimental frequencies for these fundamentals can be derived from condensed-phase spectra or from combination bands, the latter being mostly highly speculative. The frequencies for fundamentals of a_2 symmetry reported in this work are taken from the Raman spectrum of the melt since these normal modes are active in Raman scattering. The missing b_2 modes are taken from the spectrum in saturated CCl_4 solution.

Thus, in accordance with the *ab initio* predictions, the lines at 960, 790 and 395 cm^{-1} of the Raman spectrum are assigned to ν_{11}, ν_{12} and ν_{13} (a_2) modes, the first two of them consisting of combinations of γ_{CH} coordinates while $\nu_{13}(a_2)$ is the "symmetric" ring torsion, τ_3.

The observed i.r.-active fundamentals of appreciable intensity are all related to some extent to the out-of-plane motion of the carbonyl group. The *C*-type bands at frequencies of 847 and 720 cm^{-1} (Fig. 11) are assigned to $\nu_{24}(b_2)$ and $\nu_{25}(b_2)$. The experimental frequency of the asymmetric ring torsion, $\nu_{27}(b_2)$ is taken from the work of Smithson *et al.* [24] at 149 cm^{-1}. The interesting progression of bands just below 847 cm^{-1} (Fig. 11a) shows a falling off in intensity that is compatible with the series arising from the ν_{24} band in progressively higher excited states of the 149 cm^{-1} ring torsion motion ν_{27}.

A summary of the proposed assignment of the fundamentals is compiled in Table 3. The experimental frequencies taken from condensed phases (those in Table 3 with superscript R or S) are, of course, slightly different from the isolated molecule frequencies that would be observed in the gas phase. Of the two sets of *a priori* predictions (calculations I and II), calculation II based on transfer of scale factors from benzene is probably more reliable since there is a closer similarity between the reference molecule and the molecule under study. The best computational prediction from our study is calculation III, which makes use of the more certain experimental assignments for γ-pyrone to scale the force field.

FORCE FIELD

The SQM *ab initio* (4-21) force field of γ-pyrone are given in Tables 4 and 5 for the in-plane and out-of-plane vibrations, respectively.

The non-conjugative character of the γ-pyrone ring [33] is strongly reflected in the in-plane force field. The diagonal constants associated with the C=C bonds are considerably larger than those of the C–C single bonds, having values of 8.927 and 5.051 mdyne/Å,

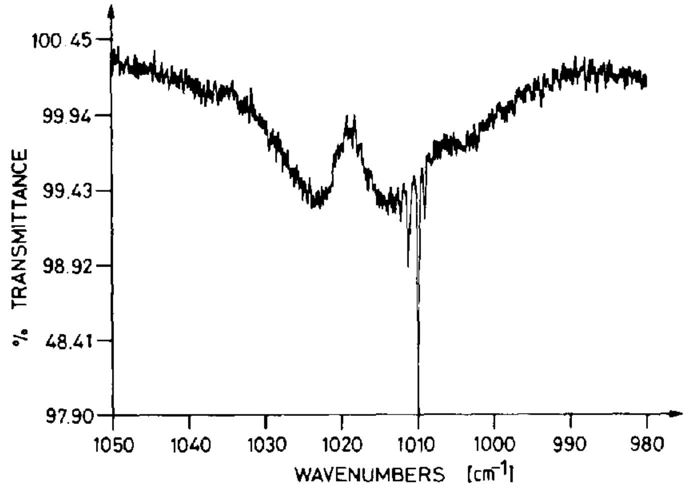


Fig. 9. The $\nu_7(a_1)$ and $\nu_{20}(b_1)$ bands of γ-pyrone in the gas-phase i.r. spectrum.

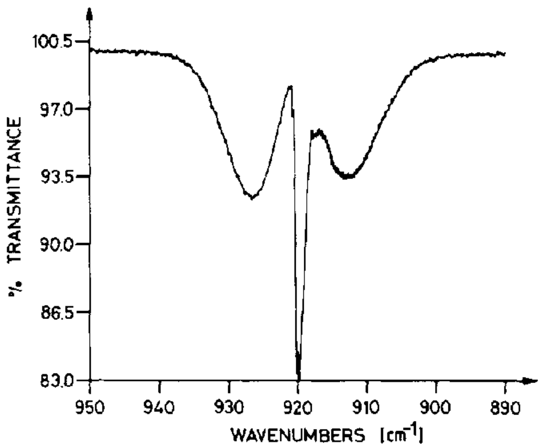


Fig. 10. The $\nu_8(a_1)$ band of γ-pyrone in the gas-phase i.r. spectrum.

respectively. The corresponding force constants for benzene [7] and for pyridine [10] have values intermediate between those above, indicating the extensive conjugation in these ring systems. The rigidness of the conjugated rings in benzene and in pyridine is also reflected in somewhat higher diagonal force constants for ring torsion in those molecules than in γ-pyrone.

The off-diagonal force constants also indicate that local couplings dominate, as was seen in an earlier CNDO/2 study [34] of maleimide and uracil, further illustrating the non-conjugative character of these molecules.

SCALE FACTORS

The values of the scale factors used in correcting the directly computed force field to obtain the SQM force

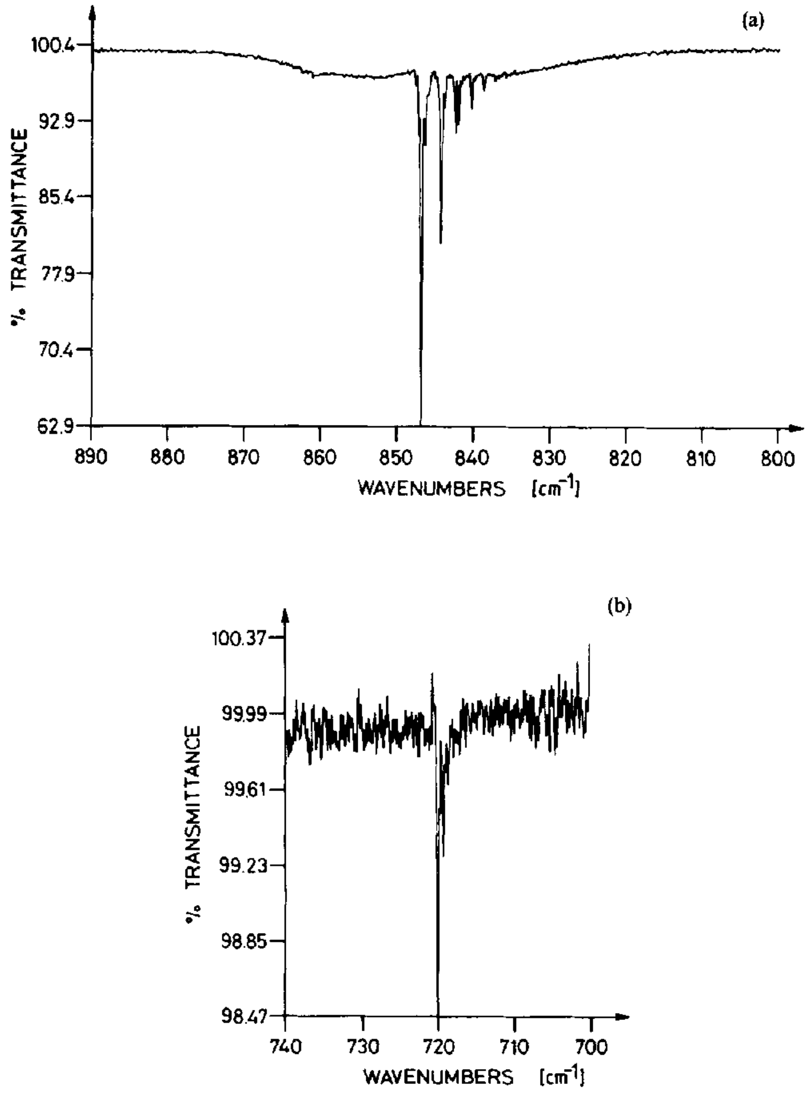


Fig. 11. The $\nu_{24}(b_2)$ and $\nu_{25}(b_2)$ bands of γ-pyrone in the gas-phase i.r. spectrum.

Table 3. Summary of the assignments of fundamentals for γ-pyrone*

				Calculated §		
No.	Symmetry	Description†	Experimental‡	I	II	III
1	a_1	ν_{CH}	3098	3106	3106	3101
2	a_1	ν_{CH}	3076^{R}	3072	3072	3067
3	a_1	$\nu_{C=O}$	1702	1678	1707	1715
4	a_1	$\nu_{C=O} + \nu_{C=C}$	1652	1607	1649	1642
5	a_1	β_{CH}	1385^{S}	1380	1373	1382
6	a_1	β_{CH}	1193	1197	1194	1201
7	a_1	$\beta_{ring} + \beta_{CH}$	1010	1006	1010	1011
8	a_1	$\beta_{CH} + \beta_{ring}$	920	898	911	908
9	a_1	ν_{CC}	825^{S}	804	811	803
10	a_1	β_{ring}	502^{S}	490	493	494
11	a_2	γ_{CH}	960^{R}	965	965	976
12	a_2	γ_{CH}	790^{R}	789	786	793
13	a_3	$\gamma_{C=O}$	395^{R}	408	401	398
14	b_1	ν_{CH}	3098	3103	3102	3098
15	b_1	ν_{CH}	3076^{R}	3072	3072	3067
16	b_1	$\nu_{C=C}$	1610^{R}	1559	1611	1590
17	b_1	$\nu_{CC} + \nu_{CO}$	1401	1406	1416	1405
18	b_1	$\beta_{CH} + \nu_{CO}$	1314	1317	1316	1322
19	b_1	$\beta_{CH} + \beta_{C=O}$	1216^{S}	1220	1220	1217
20	b_1	$\nu_{CO} + \beta_{CH}$	1019	1013	1024	1020
21	b_1	$\beta_{ring} + \nu_{CO}$	625^{S}	636	649	637
22	b_1	$\beta_{C=O} + \beta_{ring}$	458^{S}	441	456	434
23	b_2	γ_{CH}	960^{R}	959	959	970
24	b_2	$\gamma_{C=O}$	847	844	844	848
25	b_2	$\tau_{ring} + \gamma\gamma\gamma_{C=O}$	720	723	716	714
26	b_2	$\tau_{ring} + \gamma_{C=O}$	424‖	434	430	429
27	b_2	γ_{ring}	149‖	158	156	155

*Frequencies are in cm^{-1}.

†Based on the *M*-matrix [23]; for notation see Table 1.

‡From gas phase spectra of this work if not otherwise specified; upper right indices R and S denote frequencies taken from Raman spectra of the melt and i.r. spectrum of CCl_4 solution, respectively.

§Calculated by SQM force fields of calculation I, II and III. See text.

‖Taken from Ref. [17].

field are shown in Table 6. As pointed out in the earlier sections, the gas-phase i.r. spectrum of γ-pyrone was almost completely interpretable using scale factors transferred either from a set of aliphatic molecules (calculation I) or from benzene (calculation II). The mean deviation between the experimental frequencies and those obtained in calculation I is 13.4 cm^{-1} for the in-plane frequencies and 5.0 cm^{-1} for the out-of-plane frequencies. The scale factors from benzene produce a marked improvement in the in-plane modes, reducing the average deviation to only 8.8 cm^{-1}, but have little effect on the out-of-plane frequency, changing the already-small deviation of 5.0 cm^{-1} to 5.6 cm^{-1}. It should be noted that the accuracy of spectral prediction with the benzene scale factors is quite comparable to that obtained when these factors were used to predict the spectra of pyridine [8, 9], naphthalene [10] and aniline [11].

Calculation III is based on a set of scale factors refined as described above to give the best fit to the experimental data on γ-pyrone. The mean deviation of the predicted frequencies using this set of factors is 6.6 cm^{-1} for the in-plane modes and 3.9 cm^{-1} for the out-of-plane modes. The most striking point is that there is so little improvement in simply fitting the observed data (calculation III) compared with the *a priori* prediction of the spectrum (calculation II). The difference is insignificant considering the fact that the isolated harmonic oscillator approximation is used and the additional source of error in using some of the frequencies from spectra in condensed phases.

CONCLUSIONS

It is demonstrated that information gained from a relatively modest level *ab initio* calculation coupled with transfer of scale factors from other molecules to yield a scaled quantum-mechanical (SQM) force field can be used successfully in conjunction with experiment to obtain a reasonably complete and trustworthy analysis of the spectrum of a complex molecule, γ-pyrone. Unequivocal assignments were possible from the computed frequencies and intensities. The only predicted frequencies not observable in the gas-phase spectrum were those which were predicted to have such low intensity that they should not be observable. In most cases, these bands could be picked up from condensed-phase i.r. spectra or from the Raman spectrum of the melt.

Table 4. In-plane SQM force field of γ-pyrone*

r_1	5.252																		
r_2	0.013	5.183																	
r_3	0.014	0.022	11.031																
r_4	0.0	0.0	0.022	5.183															
r_5	0.0	0.0	0.014	0.013	5.252														
R_1	0.146	−0.038	0.024	−0.010	−0.053	6.202													
R_2	0.046	0.053	−0.124	−0.028	−0.011	0.622	8.927												
R_3	−0.010	−0.033	0.839	−0.008	−0.025	−0.254	0.376	5.051											
R_4	−0.025	−0.008	0.839	−0.033	−0.010	0.272	−0.075	0.307	5.051										
R_5	−0.011	−0.028	0.124	0.053	0.046	−0.092	0.038	0.075	0.376	8.927									
R_6	−0.053	−0.010	0.024	−0.038	0.146	0.288	−0.092	0.272	−0.254	0.622	6.202								
β_1	0.0	0.0	−0.012	0.0	0.005	0.347	−0.123	0.009	−0.023	−0.017	−0.021	0.530							
β_2	0.004	0.0	0.004	0.006	0.0	0.176	−0.102	0.0	0.016	−0.055	0.0	0.443							
β_3	0.006	−0.032	0.0	0.032	−0.006	0.103	−0.040	0.261	−0.261	0.040	−0.103	−0.020	0.045	1.000					
β_4	0.0	−0.006	0.004	0.0	0.004	−0.055	0.016	0.0	−0.102	0.176	0.006	0.0	0.012	−0.045	0.443				
β_5	0.005	0.0	−0.012	0.0	0.0	−0.021	−0.017	−0.023	0.009	−0.123	0.347	0.013	0.0	0.020	0.0	0.520			
q_1	0.068	−0.096	0.247	−0.096	0.068	0.199	−0.046	0.061	0.064	−0.044	0.199	0.034	0.004	0.0	0.004	0.035	1.323		
q_2	0.310	0.063	−0.350	0.063	0.031	0.308	−0.168	0.0	0.059	−0.168	0.308	0.082	−0.081	0.0	−0.081	0.081	−0.017	1.221	
q_3	−0.065	0.074	0.0	−0.074	0.065	0.300	−0.114	−0.174	0.174	0.114	−0.300	−0.019	0.056	−0.157	−0.056	0.019	0.0	0.0	1.238

*Units are consistent with energy measured in aJ, bond lengths in Å = 10^{-10} m and bond angles in radians.

For notation, see Fig. 3 and Table 1. The values listed here are obtained in calculation III, i.e. the theoretical force constants are scaled with optimized scale factors listed in column III of Table 6.

Table 5. Out-of-plane SQM force constants of γ-pyrone*

γ_1	0.429							
γ_2	−0.093	0.407						
γ_3	−0.040	−0.038	−0.648					
γ_4	−0.009	−0.010	−0.038	0.407				
γ_5	0.009	−0.009	−0.040	−0.093	0.429			
τ_1	−0.117	0.137	−0.022	0.137	−0.117	0.241		
τ_2	−0.033	−0.025	0.069	−0.025	−0.033	0.009	0.105	
τ_3	0.125	−0.165	0.0	0.165	−0.125	0.0	0.0	0.327

*See footnotes to Table 4.

Table 6. Empirical scale factors for the force constants*

Coordinate	I†	II‡	III §
ν_{CH}	0.866	0.863	0.866
$\nu_{C=O}$	0.826	0.880¶	0.855
ν_{CO}	0.856‖	0.880¶	0.888
$\nu_{C=C}$	0.866	0.911	0.939
ν_{CC}	0.920	0.911	0.938
β_{CH}	0.800	0.797	0.781
$\beta_{C=O}$	0.836	0.800¶	0.902
β_{ring}	0.800¶	0.808	0.803
γ_{CH}	0.730	0.739	0.726
$\gamma_{C=O}$	0.800¶	0.800¶	0.803
τ_{ring}	0.800¶	0.768	0.775

*The diagonal force constants obtained from *ab initio* calculation were multiplied with the scale factors listed and their geometric mean was applied to the coupling force constants [1]. For notation see Table 1.

†Taken from Ref. [1] if not otherwise specified.

‡Calculation based on the scale factors obtained for benzene [7].

§Optimized values obtained by fitting the calculated frequencies to the experimental ones.

‖From *ab initio* calculations with 4-31 basis set: for references see Ref. [1].

¶Approximate values from the consideration that the bending force constants are overestimated by ca 20% and the stretching ones by ca 12%, in calculations with 4-21 basis set.

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REFERENCES

[1] P. PULAY, G. FOGARASI, G. PONGOR, J. E. BOGGS and A. VARGHA, *J. Am. chem. Soc.* **105**, 7037 (1983).

[2] P. PULAY, in *Modern Theoretical Chemistry* (edited by H. F. SCHAEFER III). Plenum Press, New York (1977).

[3] P. PULAY, in *The Force Concept in Chemistry*, pp. 449–480 (edited by B. M. DEB). Van Nostrand Reinhold, New York (1981).

[4] G. FOGARASI and P. PULAY, *A. Rev. phys. Chem.* **35**, 191–213 (1984).

[5] G. FOGARASI and P. PULAY, in *Vibrational Spectra and Structure*, Vol. 13 (edited by J. R. DURIG). Elsevier, Amsterdam (1985).

[6] P. PULAY, G. FOGARASI, F. PANG and J. E. BOGGS, *J. Am. chem. Soc.* **101**, 2550 (1979).

[7] P. PULAY, G. FOGARASI and J. E. BOGGS, *J. chem. Phys.* **74**, 3999 (1981).

[8] G. PONGOR, P. PULAY, G. FOGARASI and J. E. BOGGS, *J. Am. chem. Soc.* **106**, 2765 (1984).

[9] G. PONGOR, G. FOGARASI, P. PULAY and J. E. BOGGS, *J. molec. Spectrosc.*, in press.

[10] H. SELLERS, P. PULAY and J. E. BOGGS, *J. Am. chem. Soc.* **107**, 6487 (1985).

[11] Z. NIU, K. M. DUNN and J. E. BOGGS, *Molec. Phys.*, in press.

[12] K. M. DUNN, P. PULAY, C. VAN ALSENOY and J. E. BOGGS, *J. molec. Spectrosc.* **103**, 268 (1984).

[13] Y. DAI, K. M. DUNN and J. E. BOGGS, *Theochem* **109**, 127 (1984).

[14] K. FAN and J. E. BOGGS, *J. molec. Struct. Theochem.*, in press.

[15] Y. XIE and J. E. BOGGS, *Molec. Phys.*, in press.

[16] P. CSÁSZÁR, A. CSÁSZÁR, L. HARSÁNYI and J. E. BOGGS, *J. molec. Struct. Theochem.*, in press.

[17] L. HARSÁNYI, P. CSÁSZÁR, A. CSÁSZÁR and J. E. BOGGS, *Int. J. Quantum Chem.*, in press.

[18] R. N. JONES, C. L. ANGELL, T. ITO and R. J. D. SMITH, *Can. J. Chem.* **37**, 2007 (1959).

[19] A. R. KATRITZKY and R. A. JONES, *Spectrochim. Acta* **17**, 64 (1961).

[20] A. R. KATRITZKY and R. J. TAYLOR, in *Physical Methods in Heterocyclic Chemistry*, Vol. 4, pp. 352–353 (edited by A. R. KATRITSZKY). Academic Press, New York (1971).

[21] P. BEAK, and G. A. CARIS, *J. org. Chem.* **29**, 2678 (1964).

[22] D. COOK, *Can. J. Chem.* **39**, 1184 (1961).

[23] D. COOK, *Can. J. Chem.* **41**, 505 (1963).

[24] T. L. SMITHSON, N. IBRAHIM and H. WIESER, *Can. J. Chem.* **61**, 1924 (1983).

[25] J. M. MACDONALD, S. A. MACKAY, J. K. TYLER, A. P. COX and I. C. EWART, *J. chem. Soc. Faraday Trans.* **77**, 79 (1981).

[26] W. PIETRZYCKI, *Roczniki Chim.* **47**, 1475 (1973).

[27] A. H. BLATT (ed.), *Organic Synthesis*, Collective Vol. 2, p. 126. Wiley, London (1943).

[28] L. SCHÄFER, *J. molec. Struct.* **100**, 51 (1983).

[29] P. PULAY, *Theor. chim. Acta* **50**, 299 (1979).

[30] P. PULAY and F. TÖRÖK, *Acta chim. acad. sci. hung.* **47**, 273 (1966).

[31] G. KERESZTURY and GY. JALSOVSZKY, *J. molec. Struct.* **10**, 304 (1971).

[32] GY. JALSOVSZKY and P. PULAY, *J. molec. Struct.* **26**, 277 (1975).

[33] Á. SOMOGYI, Z. DINYA, A. CSÁSZÁR and P. CSÁSZÁR, *J. molec. Struct.* **133**, 95 (1985).

[34] L. HARSÁNYI and P. CSÁSZÁR, *Acta chim. acad. sci. hung.* **111**, 351 (1982).