lower than the upper limits of the corresponding rate coefficients for phenyl reactions as obtained in this work. As a consequence we conclude that our upper limits may be well above the true rate coefficients and that reaction between phenyl and these compounds may only be observed at substantially higher temperatures.

The reaction of phenyl with CCl_4 my energetically occur as a simple Cl-atom metathesis reaction forming chlorobenzene + CCl_3 ($\Delta H_R = -94$ kJ/mol [29]). The low rate coefficient observed despite this exothermicity, however, is entirely consistent with the picture of phenyl as a low reactivity radical.

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References

[1] G. Porter and B. Ward, Proc. R. Soc. London *287*, 457 (1965).
[2] M. Frenklach and J. Warnatz, Comb. Sci. Techn. *51*, 265 (1987).
[3] M. Frenklach, D. W. Clary, W. C. Gardiner, and S. E. Stein, 21st Symp. (Int.) Combustion, The Combustion Institute, p. 1067, Pittsburgh 1986.
[4] D. P. Longwell, 19th Symp. (Int.) Combustion, The Combustion Institute, p. 1339, Pittsburgh 1982.
[5] J. McCann, E. Choi, E. Jamasaki, and B. N. Ames, Proc. Nat. Acad. Sci. USA *72*, 5135 (1975).
[6] J. A. Euchner, C. Venkat, K. Breszinsky, and I. Glassmann, Colloq. Int. Berthelot-Vieille-Mallard-Le Chatelier 1981, p. 290.
[7] J. C. Scaiano and L. C. Stewart, J. Am. Chem. Soc. *105*, 3609 (1983).
[8] A. Fahr and S. E. Stein, private communication.
[9] A. Fahr, W. G. Mallard, and S. E. Stein, 21st Symp. (Int.), Combustion, The Combustion Institute, p. 825, Pittsburgh 1986.
[10] R. Zellner, B. Fritz, and M. Preidel, Chem. Phys. Lett. *121*, 412 (1985).
[11] J. H. Callomon, T. M. Dunn, and I. M. Mills, Phil. Trans. R. Soc. (London) *259 A*, 499 (1966).
[12] DMS: UV-Atlas of Organic Compounds, Butterworth, London 1966.
[13] B. Cercek and M. Kongshang, J. Phys. Chem. *74*, 4319 (1970).
[14] J. Lichtscheidl and M. Getoff, Monatsh. Chem. *110*, 1367 (1979).
[15] N. Ikeda, N. Nakashima, and K. Yoshihara, J. Am. Chem. Soc. *107*, 3381 (1985).
[16] S. W. Benson, "Thermochemical Kinetics", J. Wiley 1976.
[17] K. Y. Choo, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinet. *7*, 713 (1975).
[18] T. Ebata, K. Obi, and I. Tanaka, Chem. Phys. Lett. *77*, 480 (1981).
[19] H. E. van den Bergh and A. B. Callear, J. Chem. Soc. Faraday Trans. *67*, 2071 (1971).
[20] P. H. Kasai, E. Hedaya, and E. B. Whipple, J. Am. Chem. Soc. *91*, 4364 (1969).
[21] H. Zemel and R. W. Fessenden, J. Phys. Chem. *79*, 1419 (1975).
[22] R. P. Johnson, J. Org. Chem. *49*, 4857 (1984).
[23] R. C. Weast, CRC Handbook of Chemistry and Physics, 64 ed., Boca Raton, Florida 1983.
[24] Calculated from ΔH_f ($C_6H_5NO_2$, liquid) = 18 kJ/mol [23] and ΔH_v = 68.8 kJ/mol. The ΔH_f-value for C_6H_5ONO was estimated as ΔH_f ($C_6H_5NO_2$) + 10 kJ/mol corresponding to the difference in ΔH_f-values between CH_3NO_2 and CH_3ONO.
[25] F. Yamada, I. R. Slagle, and D. Gutman, Chem. Phys. Lett. *83*, 409 (1981).
[26] W. Tsang, D. Robaugh, and W. G. Mallard, J. Phys. Chem. *90*, 5968 (1986).
[27] R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, and J. Troe, Int. J. Chem. Kinet. *21*, 115 (1989).
[28] H. E. Hunziker and H. R. Wendt, J. Chem. Phys. *60*, 4622 (1974).
[29] D. F. McMillen and D. M. Golden, Ann. Rev. Phys. Chem. *33*, 493 (1982).
[30] J. A. Kerr and S. J. Moss, "Handbook of Bimolecular and Termolecular Reactions", CRC Press, Boca Raton, Florida 1981.

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Absolute Raman Intensities of the Carbonyl Stretching Band in Para Substituted Methyl Benzoates

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Spectroscopy, Raman / Spectroscopy, Ultraviolet

The absolute Raman intensities of the $\nu_{C=O}$ band of para substituted methyl benzoates have been measured in CCl_4 solution at different excitation frequencies. The intensities depend on a preresonance Raman effect (PRRE) and are correlated with theoretical expressions which describe the dispersion of the Raman intensity as a function of the excitation frequency and the experimental UV frequencies of the compounds, in particular the $\pi \rightarrow \pi^*$ ^1L_a band. — The Raman intensities free from PRRE are deduced by extrapolating the experimental values to a zero excitation frequency. These extrapolated intensities depend on the electron donating character of the substituents and on the extent of the conjugated system. — The depolarization ratio of the $\nu_{C=O}$ band in methyl benzoates increases with the excitation energies, this ratio is higher for the para substituted derivatives.

Introduction

In previous works we have been concerned with the influence of hydrogen bonding on the Raman intensity of the $\nu_{C=O}$ band in aliphatic esters [1,2] and ketones [3,4]. It was shown that the intensity increased on hydrogen bonding. From other literature data it is clear that the Raman intensity is very sensitive to conjugation effects [5–13]. To have a better understanding on the effect of conjugation on the Raman intensity of the $\nu_{C=O}$ band, the effect of para substitution on the Raman intensity of the $\nu_{C=O}$ band in

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methyl benzoates is investigated. Thompson et al. measured the Raman intensities of substituted methyl benzoates using the Hg line at 4358 Å; the Raman intensities were shown to be dependent on the UV absorption frequencies [10].

The influence of hydrogen bonding on the $\nu_{C=O}$ band of the same molecules will be presented in a subsequent paper.

Experimental

Raman spectra have been recorded on a Coderg T800 spectrophotometer equipped with a Tracor Northern Multichannel Analyser TN-1750. Five different lines from a Spectra Physics 164 Ar^+ or Kr^+ laser were used: 647.1 nm (Kr^+), 514.5 nm (Ar^+), 488.0 nm (Ar^+), 476.5 nm (Ar^+) and 350.7 nm (Kr^+). For the excitation with the 488.0, 514.5 and 647.1 nm lines a power of 500 mW was used, for the 476.5 nm line 100 mW and for the 350.7 nm line 30 mW.

To determine the absolute Raman intensity the method of the internal standard was used. The internal standard was in most cases the $\nu_{C=O}$ band of cyclohexane at 1654 cm^{-1}. However for the 350.7 nm excitation the 217 cm^{-1} band of CCl_4 was used as standard since this band does not show preresonance Raman enhancement in this energy range [14]; whereas the $\nu_{C=O}$ band of cyclohexene is expected to be slightly preresonance Raman enhanced for the 350.7 nm excitation.

The relative intensity has been determined by comparing the band areas of the $\nu_{C=O}$ band and the standard band for a normalized standard concentration (0.15 mol dm^{-3} for cyclohexene). If the ratio $I_{\nu_{C=O}}/I_{ST}$ is divided by the C=O concentration, the relative molar intensity, I^0, is obtained. The ratio of the absolute Raman intensities is given by

$$S = (I_R^0)\, C_{ST}\, \frac{\sigma_{C=O}}{\sigma_{ST}}\, \frac{\nu_{C=O}}{\nu_{ST}}\, \frac{(\nu_0-\nu_{ST})^4}{(\nu_0-\nu_{C=O})^4}\, \frac{(1-e^{-h\nu_{C=O}/kT})}{(1-e^{-h\nu_{ST}/kT})}$$

where C_{ST} is the normalized standard concentration and ν_0 is the excitation frequency. For every excitation energy the intensities were corrected for the spectral sensitivity of the photomultiplier ($\sigma_{C=O}/\sigma_{ST}$). The relative absolute intensity of the internal standard to the ν_1 band of CCl_4 has been determined while the absolute Raman intensity of the latter is $20.25 \cdot 10^{-32}$ cm^4 amu^{-1} [15]. The standard deviation on the absolute Raman intensities was between 5 and 10%.

To determine the depolarization ratio the spectra were scanned with a parallel and perpendicular analyser placed between the cell and the collecting lens of the spectrophotometer. We used a polarization scrambler in order to eliminate the different efficiency of the instrument for the two polarizations. This scrambler was calibrated for the frequency dependence.

The concentration of the benzoates was strongly dependent on the experimental conditions and ranged from 0.05 to 1 mol dm^{-3}.

The UV spectra were measured on a Beckman 35 UV-visible spectrophotometer. The benzoate concentration in hexane ranged between 10^{-5} and 10^{-4} mol dm^{-3}.

Most of the para substituted methyl benzoates from Janssen Chimica or Fluka were recrystallized. Methyl benzoate has been vacuum distilled. The para fluoro, bromo, iodo and phenyl derivatives have been synthesized from the corresponding acids in methanol with sulphuric acid as catalyst. Cyclohexene (Fluka purum) was distilled before use.

Results and Discussion

1. Raman Intensity of the $\nu_{C=O}$ Band

The absolute Raman intensity is defined by the expression $(45\bar{\alpha}'^2 + 7\gamma'^2 + 5\delta'^2)$. $\bar{\alpha}'$ represents the mean polarizability derivative, γ'^2 the anisotropy and δ'^2 the asymmetry derivative:

$$\bar{\alpha}' = 1/3\,(\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz})_0$$

$$\gamma'^2 = 1/2\,[(\alpha'_{xx} - \alpha'_{yy})_0^2 + (\alpha'_{yy} - \alpha'_{zz})_0^2 + (\alpha'_{zz} - \alpha'_{xx})^2 + 6(\alpha'_{xy} + \alpha'_{yz} + \alpha'_{zx})_0]$$

$$\delta'^2 = 3/4\,[(\alpha'_{xy} - \alpha'_{yx})_0^2 + (\alpha'_{xz} - \alpha'_{zx})_0^2 + (\alpha'_{yz} - \alpha'_{zy})_0^2]\,.$$

In normal Raman scattering the polarizability tensors are symmetric and $\delta'^2 = 0$.

Table 1
Raman data (frequencies and intensities) for the $\nu_{C=O}$ band of 4-substituted methylbenzoates. Solvent = CCl_4. T^0 = 298 K

Substituent	$\nu_{C=O}$ *)	Absolute raman intensity**) 15455	19436	20492	20986	28514/cm^{-1}
H	1729	40.1	50.7	53.4	61.6	98.3
F	1731	46.1	59.5			
NO_2	1736	51.4	62.1			
CN	1736	56.5	70.8			
Cl	1731	58.8	75.9			
Br	1733	66.9	90.3			
$C(CH_3)_3$	1728	65.6	94.5			216
I	1733	73.6	116			
OCH_3	1723	87.8	127	138	165	468
Phenyl	1729	100	177			882
$N(CH_3)_2$	1709	232	405	460	491	

*) In cm^{-1}; **) in 10^{-32} cm^4 amu^{-1}.

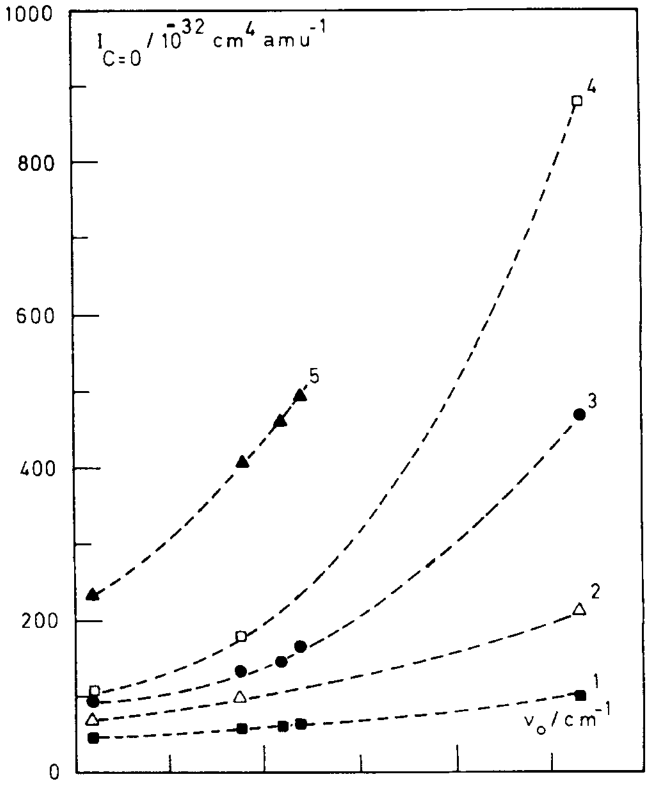

Fig. 1
Absolute Raman intensity of the $\nu_{C=O}$ band in 4-substituted methyl benzoates as a function of the excitation frequency.
Substituents: 1: H; 2: $C(CH_3)_3$; 3: OCH_3; 4: C_6H_5; 5: $N(CH_3)_2$

Table 1 shows that the Raman intensity of the $\nu_{C=O}$ band in methyl benzoate depends on the nature of the substituent in para position. As a result of a preresonance Raman effect the influence of the substitution is more pronounced for the higher excitation frequencies. This is illustrated in Fig. 1.

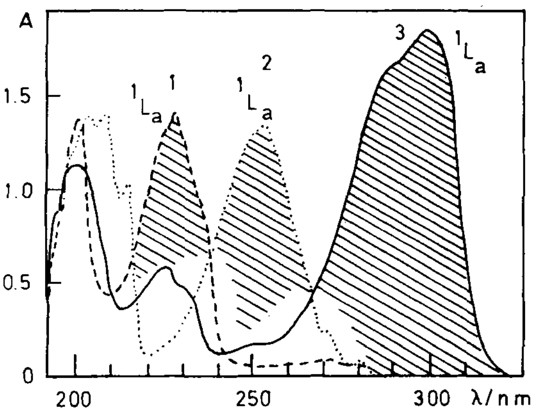

Fig. 2
UV spectrum (200—300 nm) of some 4-substituted methyl benzoates (solvent = hexane).
Substituents: 1: H ($c = 1.2\cdot10^{-4}$ M)
2: OCH_3 ($c = 7.2\cdot10^{-5}$ M)
3: $N(CH_3)_2$ ($c = 6.5\cdot10^{-5}$ M)

Table 2
UV data (cm^{-1}) for the para substituted methyl benzoates (S = hexane)

Substituent	^1L_a*)	$^1B_{a,b}$
H	43960	50505
F	43570	49830
NO_2	39220	50250
CN	41870	50500
Cl	41840	49630
Br	41020	49380
$C(CH_3)_3$	42280	49570
I	39220	50760
OCH_3	39530	49020
Phenyl	37170	49860
$N(CH_3)_2$	33440	50120/44440

*) These values are 200—500 cm^{-1} higher than those reported by Thompson [10] where S = CH_3OH.

Table 3
Experimental preresonance Raman enhancement factors, relative F_A^2 and F_B^2 frequency factors with reference to ν_0 = 15455 cm^{-1}

ν_0/cm^{-1}	Methyl benzoate			Methyl 4-OCH_3 benzoate		
	I_{REL}	$(F_B^2)_{REL}$	$(F_A^2)_{REL}$	I_{REL}	$(F_B^2)_{REL}$	$(F_A^2)_{REL}$
15455	1.00	1.00	1.00	1.00	1.00	1.00
19436	1.26	1.19	1.59	1.45	1.25	1.81
20492	1.33	1.25	1.84	1.57	1.34	2.18
20986	1.54	1.29	1.98	1.88	1.39	2.40
28514	2.45	2.29	8.38	5.33	3.12	16.9

The important intensification of the $\nu_{C=O}$ band in the para substituted methyl benzoates is accompanied by a red shift of the ^1L_a ($\pi\rightarrow\pi^*$) band in the UV spectrum. This is shown in Table 2 and Fig. 2. It is a first indication that the ^1L_a state is playing an important role in the Raman intensity of the $\nu_{C=O}$ band in the benzoate derivatives. The relation with other $\pi\rightarrow\pi^*$ transitions is less clear. There seems to be no correlation with the ^1B *band(s) at higher wavenumbers*, while the lower lying ^1L_b band is very weak and usually difficult to localize owing to strong overlap with the much more intense ^1L_a band.

In the semiclassical theory of Shorygin [8, 16, 17], the polarizability derivative taken with respect to the normal coordinate Q can be expressed by the equation

$$\left(\frac{\delta\alpha}{\delta Q}\right)_0 = C^{ste}\sum_e\left(\frac{\delta M_e}{\delta Q}\right)_0^2\frac{\nu_e}{\nu_e^2-\nu_0^2}$$

$$-M_e^2\left(\frac{\delta\nu_e}{\delta Q}\right)_0\frac{\nu_e^2+\nu_0^3}{(\nu_e^2-\nu_0^2)^2}$$

where M_e is the amplitude of the transition moment associated with the transition, ν_e the frequency of the electronic transition responsible for the Raman preresonance enhancement and ν_0 the frequency of the incident light.

The frequency factors are

$$F_A = \frac{\nu_e^2+\nu_0^2}{(\nu_e^2-\nu_0^2)^2}$$

$$F_B = \frac{\nu_e}{\nu_e^2-\nu_0^2}\,.$$

In the more sophisticated approach of Albrecht [18—20] allowance is made for two excited electronic states.

Fig. 3a shows that for methyl benzoate the preresonance Raman effect can successfully be described with the factor

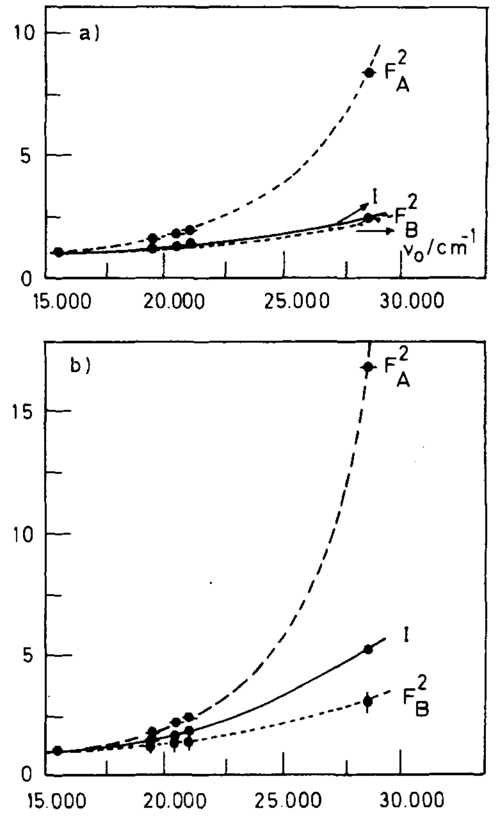

Fig. 3
Relative intensity increase of the $\nu_{C=O}$ band as a function of the F_A^2 and F_B^2 factors relative to their values at ν_0 = 15455 cm^{-1}.
a) methyl benzoate; b) 4-OCH_3 methyl benzoate

F_B^2 alone. For benzoates with strong interacting substituents like OCH_3 or $N(CH_3)_2$ the excitation profile is shown in Fig. 3b: the relative increase of the intensity is also closer to the relative variation of F_B^2. However, the experimental values are somewhat higher. This may result from an enhanced participation of the F_A^2 factor which increases much faster than F_B^2 and which becomes predominant near the resonance condition. The slight deviation from the F_B^2 curve is also possibly due to the approximations used in the quantum mechanical expression for the dispersion of the Raman intensity. The Raman intensity of the $\nu_{C=O}$ band in benzoyl derivatives can also satisfactorily be described by use of the F_B^2 frequency factor alone [7].

Table 4
Extrapolated intensities for $\nu_0 = 0\ cm^{-1}$ and the electrophilic substituent constants σ_p^+ [21–23]

Substituent	$I'_{C=O}$	σ_p^+
H	32.7	0
F	30.8	−0.07
Cl	39.1	0.12
Br	41.1	0.16
$C(CH_3)_3$	47.5	−0.27
OCH_3	49.3	−0.75
Phenyl	48.6	−0.18
$N(CH_3)_2$	107	−1.7
NO_2	38.8	0.78
CN	40.2	0.71

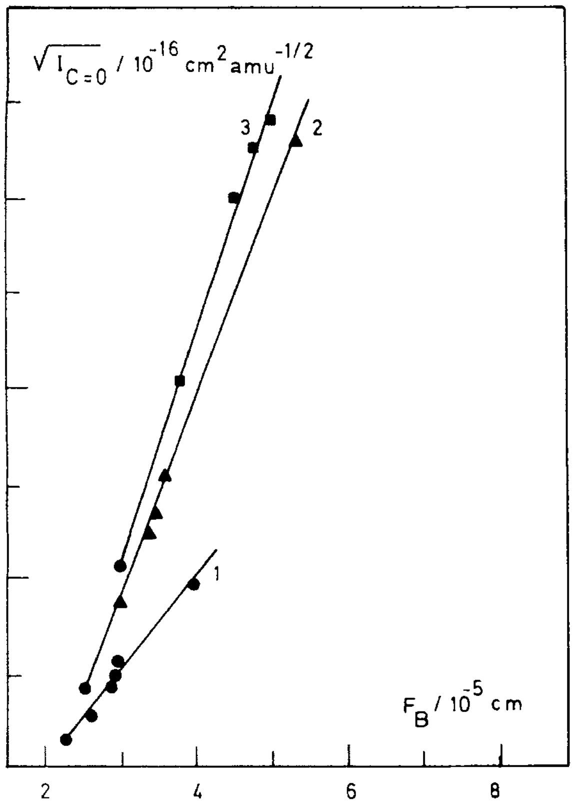

Fig. 4
Square root of the Raman intensity of the $\nu_{C=O}$ band as a function of F_B.
Substituents: 1: H; 2: OCH_3; 3: $N(CH_3)_2$

The intensities corrected for the frequency factor can be obtained by plotting the square root of the absolute Raman intensity as a function of $F_B = \nu_e/(\nu_e^2 - \nu_0^2)$ and by extrapolating these points to the value characterized by $F_B = 1/\nu_e$ ($\nu_0 = 0\ cm^{-1}$). This procedure is illustrated for methyl benzoate and the para methoxy and para dimethylamino derivatives (Fig. 4). The corrected Raman intensities for the studied benzoates are listed in Table 4.

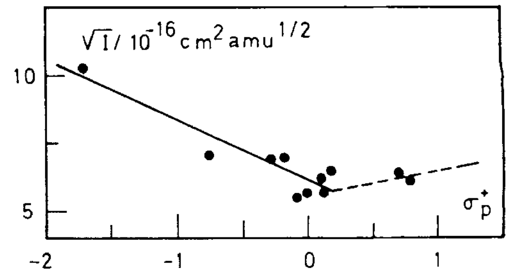

Fig. 5
Square root of the Raman intensity of the $\nu_{C=O}$ band as a function of σ_p^+

The Raman intensities obtained in this way can be related to the nature of the chemical bond in the ground state. They have been shown to be very sensitive to conjugation effects [7,24]. Fig. 5 shows the correlation between the Raman intensities free from preresonance effect and the electrophilic substituent constants σ^+. For the NO_2 and CN derivatives the intensities are still higher than for the non substituted methyl benzoate. Also the phenyl group shows a relatively high value in comparison to its σ^+ value. These effects can be explained by considering the extent of the conjugation over the whole molecule. Although the NO_2 and CN groups are strongly electron withdrawing and consequently they have a large σ_p^+ value, these substituents increase the length of the conjugated system and as a consequence increase the overall polarizability of the molecule. A quantitative approach of this effect is difficult. However, Schmid et al. have proposed approximative values to describe the length of the conjugated system in monosubstituted benzenes and di-

Table 5
Raman data (frequencies and intensities) for the $\nu_{8a,b}$ band of 4-substituted methyl benzoates. Solvent = CCl_4. T^0 = 298 K

Substituent	$\nu_{8a,b}$*)	Absolute raman intensity**) 15455	 19436	 20492	 20986/cm^{-1}
H	1604	18.2	30.3	40.4	54.7
F	1603	17.0	29.7		
NO_2	1604	78.5	130		
CN	1612	64.1	102		
Cl	1599	40.8	71.5		
Br	1593	40.2	83.7		
$C(CH_3)_3$	1611	48.6	93.8		
I	1588	59.2	105		
OCH_3	1609	80.3	134	157	188
	1582				
$N(CH_3)_2$	1610	279	560	723	
	1582				

*) In cm^{-1}; **) in $10^{-32}\ cm^4\ amu^{-1}$.

phenylpolyenes [7]. They have shown that after correction has been made for the preresonance Raman effect, the intensity of the $\nu_{8a,b}$ vibration is related to the length of the conjugated system but strong deviations were observed for substituents with strong electronic interaction. In our work similar conclusions can be drawn for the Raman intensity of the $\nu_{C=O}$ band in para substituted methyl benzoates. After correction for the preresonance Raman effect the intensities are dependent on the electronic substituent effect but also on the extent of the conjugated system.

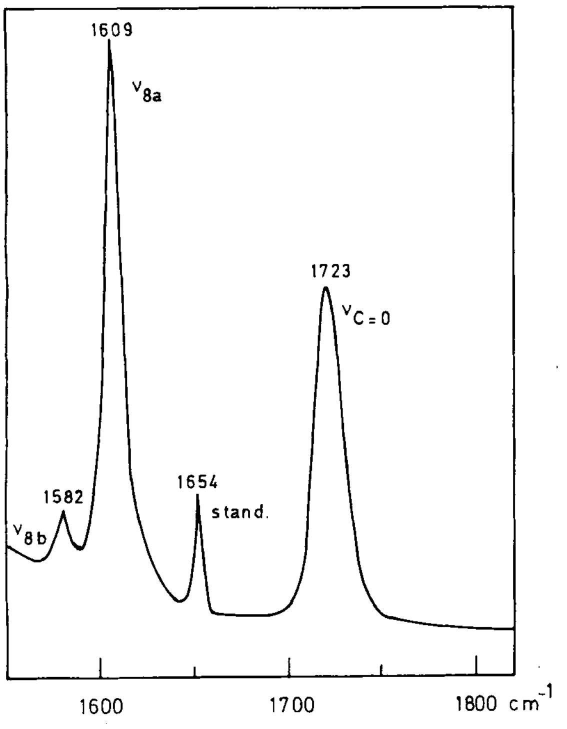

Fig. 6
Raman spectrum (1550–1800 cm^{-1}) of 4-OCH$_3$ methyl benzoate (c = 0.37 M) in the $\nu_{C=O}$ and $\nu_{8a,b}$ region (c_{st} = 0.24 M)

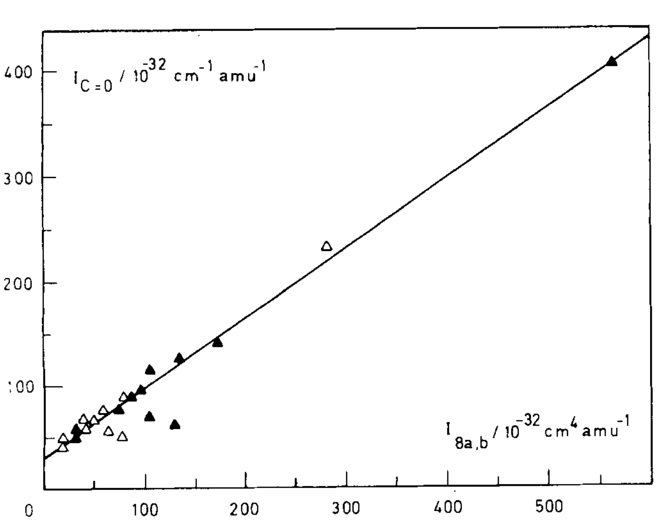

Fig. 7
Raman intensity of the $\nu_{C=O}$ band as a function of the intensity of the $\nu_{8a,b}$ band.
ν_0 = 15455 cm^{-1} (△); ν_0 = 19436 cm^{-1} (▲)

2. Raman Intensity of the $\nu_{8a,b}$ Vibration

Table 5 lists the experimental Raman intensities of the $\nu_{8a,b}$ band measured with different exciting lines. These results show that the preresonance Raman effect also influences the intensities of these ring vibrations. The linear correlation observed between the intensities of the $\nu_{C=O}$ and $\nu_{8a,b}$ bands measured with two exciting frequencies strongly suggests that both vibrations are influenced by a common factor, probably the frequency and intensity of the ^1L_a band. The $\nu_{8a,b}$ vibration plays an important role in the vibronic coupling between the ^1L_a and ^1B states [25–33] and consequently, they are expected to be very sensitive to the frequency of the exciting line. It has been shown that the ν_8 vibrations are predominant in the resonance Raman spectra of alkyl benzenes and aromatic amino acids if the excitation frequency is close to the ^1L_a frequency [28, 31]. In benzene derivatives with a symmetry different from D_{3h} or D_{6h}, the $\nu_{8a,b}$ (e_{2g}) vibrations are not degenerate. It must be pointed out however that the ν_{8a} band is much more intense and in most of the para substituted methyl benzoates, the ν_{8b} cannot be observed.

3. Depolarization Factor

If the exciting frequency approaches that of an electronic transition, the scattering tensor becomes asymmetric. In this case, the depolarization factor takes the general form

$$\varrho = \frac{3\gamma'^2 + 5\delta'^2}{34\bar{\alpha}'^2 + 4\gamma'^2}\,.$$

The dispersion of the depolarization factor can be accounted for by the asymmetric term which is zero in normal Raman scattering.

Experimental data on the depolarization factors near the resonance conditions are very limited [30, 34–36]. Table 6 and Fig. 8 illustrate the dispersion of the depolarization ratio of the $\nu_{C=O}$ band in the investigated molecules.

Table 6
Depolarization factor of the $\nu_{C=O}$ band in para-substituted methyl benzoates for the excitation frequencies 15455 cm^{-1} and 19436 cm^{-1}

Substituent	$\varrho^{C=O}$ (15455 cm^{-1})	$\varrho^{C=O}$ (19436 cm^{-1})
H	0.13	0.22
F	0.13	0.22
NO$_2$	0.13	0.22
CN	0.13	0.22
Cl	0.14	0.23
Br	0.15	0.26
C(CH$_3$)$_3$	0.15	0.24
I	0.17	0.28
OCH$_3$	0.18	0.27
Phenyl	0.18	0.28
N(CH$_3$)$_2$	0.21	0.31

From Fig. 4 it is clear that for methyl benzoate the Raman intensity measured with an excitation wavenumber of 15455 cm^{-1} is not very different from the corrected intensity, free from the preresonance Raman effect (ν_0 = 0 cm^{-1}). In the assumption that in that case $\delta'^2 = 0$, we calculate that for

$\nu_0 = 15455\ \mathrm{cm}^{-1}$, $\bar{\alpha}'^2$ and γ'^2 are respectively 0.65 and $1.54 \cdot 10^{-32}\ \mathrm{cm}^4\ \mathrm{amu}^{-1}$. If it is assumed that $\bar{\alpha}'^2$ and γ'^2 remain unchanged on going from $\nu_0 = 15455\ \mathrm{cm}^{-1}$ to $\nu_0 = 19436\ \mathrm{cm}^{-1}$ then the difference in absolute intensity for the two excitation wavenumbers is equal to $5\delta'^2 = 10.6 \cdot 10^{-32}\ \mathrm{cm}^4\ \mathrm{amu}^{-1}$. This leads to a calculated value for the depolarization ratio of 0.40 while the experimental value for $\nu_0 = 19436\ \mathrm{cm}^{-1}$ is only 0.22. Consequently the dispersion of the Raman intensity and the depolarization factor cannot be explained by taking only the δ'^2 term into account. This suggests that also the relative values of the mean polarizability components and/or the anisotropy components change on using a different excitation energy. This can be understood by considering the fact that, as we have show, the ^1L_a transition contributes to the Raman intensity of the $\nu_{C=O}$ band in the benzoates. The higher the excitation frequency, the more important will be this contribution. It is known that in the ^1L_a state the molecules are polarized along the axis between the substituents. This means that an increasing contribution of the ^1L_a state as the excitation frequency approaches the ^1L_a band, will lead to a change in the polarizability direction, namely the polarizability along the axis of the substituents is enhanced. However it is not possible to describe this effect quantitatively because it cannot be separated from the possible increase in the asymmetry of the polarizability tensor.

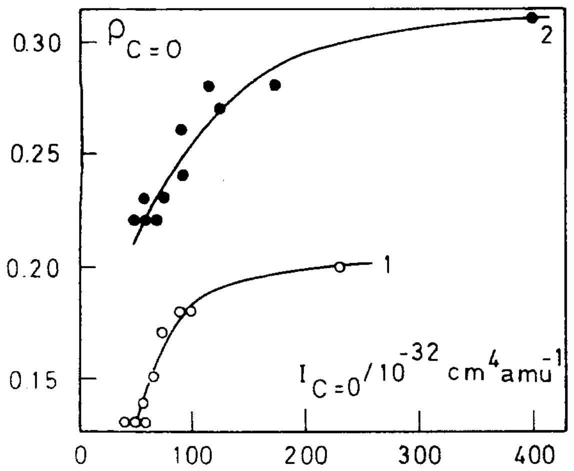

Fig. 8
Depolarization ratio of the $\nu_{C=O}$ band as a function of the Raman intensities measured for (1) $\nu_0 = 15455\ \mathrm{cm}^{-1}$ and (2) $\nu_0 = 19436\ \mathrm{cm}^{-1}$

References

[1] L. Vanderheyden and Th. Zeegers-Huyskens, J. Mol. Liquids *25*, 1 (1983).
[2] L. Vanderheyden and Th. Zeegers-Huyskens, Spectrosc. Lett., accepted for publication.
[3] C. Thijs and Th. Zeegers-Huyskens, Bull. Soc. Chim. Belg. *87*, 857 (1978).
[4] C. Thijs and Th. Zeegers-Huyskens, Spectrochim. Acta *40A*, 1057 (1984).
[5] E. D. Schmid and E. Brosa, Ber. Bunsenges. Phys. Chem. *75*, 1334 (1971).
[6] E. D. Schmid, P. Schlenker, and R. R. M. Brand, J. Raman Spectrosc. *6*, 314 (1977).
[7] E. D. Schmid and R. D. Topsom, J. Am. Chem. Soc. *103*, 1628 (1981).
[8] P. P. Shorygin, Usp. Khim. *40*, 694 (1971).
[9] G. Michel and M. Renson, Spectrochim. Acta *23A*, 1435 (1967).
[10] J. P. Jesson and H. W. Thompson, Proc. R. Soc. A *268*, 68 (part I); *268*, 79 (part II) (1962).
[11] Z. Zheng, S. Higuchi, and S. Tanaka, Spectrosc. Lett. *15*, 773 (1982).
[12] Z. Zheng, S. Higuchi, and S. Tanaka, Spectrosc. Lett. *16*, 335 (1983).
[13] C. Thijs and Th. Zeegers-Huyskens, Spectrochim. Acta *38A*, 1073 (1982).
[14] J. Behringer, in: Raman Spectroscopy, ed. H. Szymanski, Vol. 1, Chapter 6, 180 (1967).
[15] G. W. Chantry and R. A. Plane, J. Chem. Phys. *32*, 319 (1959).
[16] P. P. Shorygin, Russ. Chem. Rev. *47*, 907 (1978).
[17] P. P. Shorygin, Zh. Fiz. Khim. *21*, 1125 (1947).
[18] A. C. Albrecht, J. Chem. Phys. *34*, 1476 (1961).
[19] A. C. Albrecht and M. C. Hutley, J. Chem. Phys. *55*, 4438 (1971).
[20] J. Tang and A. C. Albrecht, Raman Spectroscopy, ed. H. Szymanski, Vol. 2, Chapter 2 (1970).
[21] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc. *79*, 1913 (1957).
[22] H. C. Brown and Y. Okamoto, J. Am. Chem. Soc. *80*, 4980 (1958).
[23] Y. Okamoto and H. C. Brown, J. Org. Chem. *22*, 485 (1957).
[24] E. D. Schmid and B. Brosa, J. Chem. Phys. *58*, 3871 (1973).
[25] N. Ohta and M. Ito, Chem. Phys. *24*, 175 (1977).
[26] N. Ohta and M. Ito, Chem. Phys. *20*, 71 (1977).
[27] L. D. Ziegler and A. C. Albrecht, J. Chem. Phys. *70*, 2644 (1979).
[28] L. D. Ziegler and B. S. Huobor, J. Chem. Phys. *79*, 1134 (1983).
[29] S. A. Asher and C. R. Johnson, J. Phys. Chem. *89*, 1375 (1985).
[30] L. D. Ziegler and B. Hudson, J. Chem. Phys. *74*, 982 (1981).
[31] R. P. Rava and T. G. Spiro, J. Phys. Chem. *89*, 1856 (1985).
[32] G. Marconi, J. Raman Spectrosc. *14*, 28 (1983).
[33] G. Marconi, J. Mol. Struct. *93*, 289 (1983).
[34] J. Behringer, in: Raman Spectroscopy, ed. H. Szymanski, Vol. 1, Chapter 6, 187 (1967).
[35] H. H. Eysel and H. J. Bernstein, J. Raman Spectr. *6*, 140 (1977).
[36] M. T. Bourgeois, U. Jacon, D. Van Labeke, and H. H. Eysel, J. Raman Spectrosc. *6*, 146 (1977).

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