Singlet–Triplet Absorption Spectra of Some Aromatic Molecules in Gas Matrices at 10 K

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Singlet–triplet transitions of some aromatic compounds have been investigated in oxygen matrices at 10 K. The technique developed in this study circumvents experimental difficulties of the classical high pressure technique of oxygen perturbation. It also overcomes the problem of estimating an accurate profile for the contact charge-transfer spectrum in the subtraction procedure by its actual measurement during the experiment. Vibrational progressions are not always lost for the studied aromatic compounds at the temperature employed and the data obtained for toluene at low temperatures may be used to add further support to recent interpretations of non-radiative rate constant data. Xenon matrix experiments indicated that the " heavy atom " effect of the gas is insufficient to produce perturbed singlet–triplet spectra at 10 K.

Information regarding the lowest triplet state of non-phosphorescent molecules is obtainable by relatively few experimental techniques;

(1) Direct observation of the singlet–triplet transition is difficult because of its spin-forbidden nature. Cells of long pathlength require high compound concentrations, which present solubility and impurity problems.[1] (An impurity of 1 p.p.m. may give rise to absorption bands with similar intensity to the expected singlet–triplet absorption spectrum). Similarly, five centimetre thick crystals of benzene at 4.2 K have been studied [2] but the procedure clearly requires extensive compound purification.

(2) Indirect methods have been successfully studied in the perturbation of spin-forbidden transitions by use of: (*a*) paramagnetic species, such as oxygen,[3, 4] nitric oxide [3b, 5] or metal ions;[6] (*b*) solvents containing heavy atoms.[7] Alternatively, fairly sophisticated experiments utilising intense light sources have been investigated in the observation of singlet–triplet transitions.

In experiments where $S_0 \rightarrow T_1$ spectra of aromatic molecules can be observed valuable data may be obtained concerning the lowest triplet state. The triplet state energy,[8] the radiative lifetime [9] and the geometry (obtained from vibronic analysis) can in principle be obtained from S_0–T_1 absorption spectroscopy. Furthermore, the rate constant for S_1–T_1 intersystem crossing in aromatic molecules has been shown to be sensitive to vibrational progressions in the triplet state.[10] However, little information is available on these triplet state vibrational frequencies.

The oxygen or nitric oxide perturbation method introduced by Evans [8] subjects the pure liquid, concentrated solution or vapour of the aromatic compound to a high applied gas pressure (150-200 atm). Spectra are taken under (*a*) atmospheric pressure conditions, (*b*) perturbed conditions, (*c*) after release of the gas (to check for the formation of secondary products). Absorptions due to the lowest triplet state are observed on the long wavelength tail of the contact charge-transfer spectrum. The singlet–triplet absorption profile is then evaluated by subtraction of the atmos-

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pheric absorption spectrum from the high pressure gas spectrum. Although this has probably represented the most convenient method for the determination of the triplet state energy of non-phosphorescent molecules, it suffers from certain inherent disadvantages; (a) the high gas pressures used may always lead to the possibility of explosion.[11] (b) Solvent–solute interactions may cause spectral shifts and modifications of the potential energy surfaces of ground and excited states.[1] (c) Well-resolved vibrational progressions of the triplet state, which may be expected in the vapour phase, are often lost.[4a] (d) Absorption due to the associated contact charge-transfer band can cover the weak singlet–triplet absorption. Its effect is generally estimated in the evaluation of the final spectrum.[3, 4, 12, 13] (e) Unless the lowest singlet and triplet states have a large energy separation the relative strength of the $S_0 \rightarrow S_1$ transition may obliterate the $S_0 \rightarrow T_1$ spectrum. This generally limits the applicability of the technique to the observation of the lowest triplet state.

It will be shown that studies in oxygen matrices at 10 K afford an extension to the indirect perturbation methods discussed above. The procedure (i) overcomes the experimental difficulties associated with the high pressure technique, (ii) indicates that vibrational progressions for the simpler aromatic molecules studied are not always lost at low temperatures and (iii) utilises the actual absorption profile of the contact charge-transfer spectrum (rather than its estimate) in the evaluation of the singlet–triplet spectrum.

Evidence for the enhancement of singlet–triplet transition probabilities of certain aromatic molecules in krypton and xenon matrices has been obtained at 4 K by Robinson.[14] Therefore an attempt at actual observation of singlet–triplet spectra of the compounds studied in oxygen matrices was carried out using xenon matrices at 10 K.

EXPERIMENTAL

Cryogenic temperatures were obtained using an Air Products Displex CSA-202 closed-cycle helium refrigeration system. The basic design for low temperature spectroscopic studies is now familiar [15] but it is relevant to describe refinements which we found essential for this work. (i) All matrices were deposited by the pulsed method of Rochkind [16] using LiF central and outer windows. (ii) The volume for pulsing the sample was 10 cm³, utilising low pressures (10-100 Torr) of matrix mixtures. (iii) After each pulse the associated sublimation pressure was allowed to subside and the temperature permitted to return to 10 K before desposition of the next pulse. These conditions repeatedly produced non-scattering matrices in the u.v. region as discussed in our previous report on contact charge-transfer interactions between aromatic molecules and oxygen at low temperatures.[17]

The matrix gases, O_2, Xe, Ar and NO were B.O.C. grade " X " purity. Benzene and toluene were purchased from B.D.H. (Research grade, 99.9 % minimum purity), as was styrene (99.5 % purity by g.l.c.). Para-difluorobenzene (PDFB) was purchased from Fluorochem (>99 % purity) and para-fluorotoluene (PFT) from Koch Light (99.5 % purity). Untraviolet spectra were recorded on a Pye Unicam SP1800B spectrometer.

RESULTS

Evaluation of the singlet–triplet absorption spectrum for benzene was carried out by two methods; (a) point by point subtraction (1 nm intervals) of an *estimated* profile for the aryl-oxygen charge-transfer spectrum from the final absorption spectrum (*i.e.*, the procedure used in the high pressure technique),[12] (b) point by point subtraction (1 nm intervals) of the *actual* contact charge-transfer profile from the final absorption spectrum. The actual contact charge-transfer profile was obtained by measuring the charge-transfer absorption spectrum after the deposition of only three pulses, when singlet–triplet absorption is negligible. The three pulse
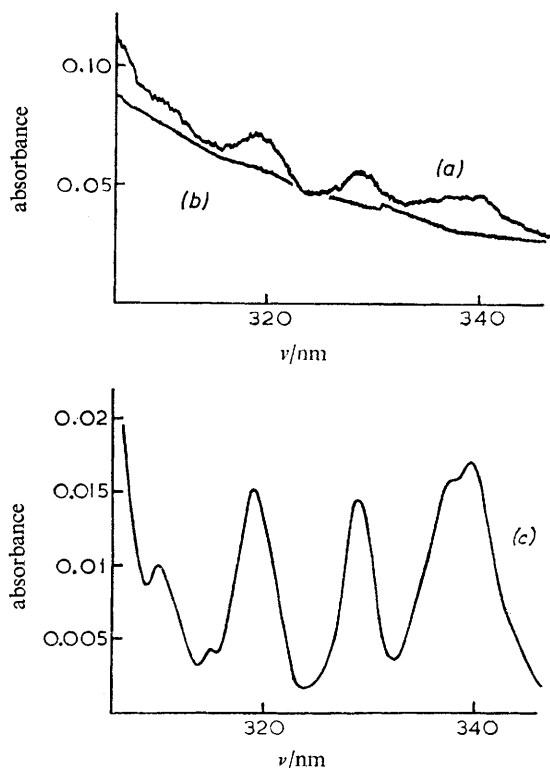
SINGLET-TRIPLET ABSORPTION

FIG. 1.—Singlet–triplet spectrum of benzene at 10 K [see text for an explanation of the lettering (*a*), (*b*), (*c*)].
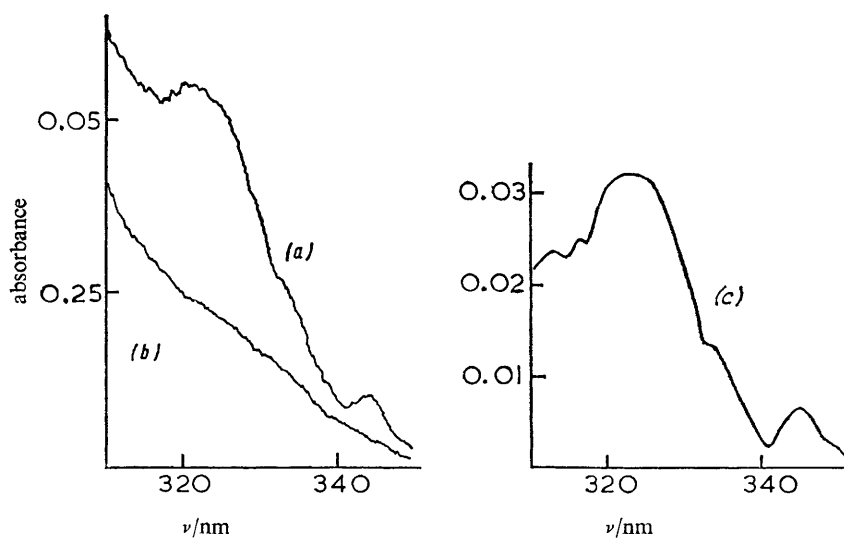

FIG. 2.—Singlet–triplet spectrum of toluene at 10 K [see text for an explanation of the lettering (*a*), (*b*), (*c*)].

absorption was then used to obtain the charge-transfer contribution after thirty pulses by normalising. Using this technique, the charge-transfer contribution was measured under exactly the same conditions (same gas mixture and same deposition conditions) as were used to obtain the total spectrum (charge transfer plus singlet–triplet absorption). Corrections for residual absorption by oxygen were found to be necessary only in the higher energy regions of the spectrum, as discussed previously.[17] Method (b) appeared to be the most satisfactory treatment of the data and was applied to the remaining aromatic compounds.
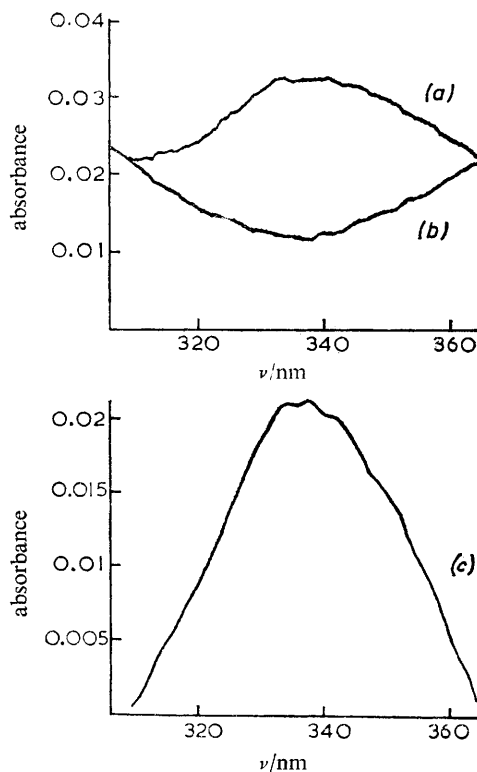

FIG. 3.—Singlet–triplet spectrum of p-difluorobenzene (PDFB) at 10 K [see text for an explanation of the lettering (a), (b), (c)].

A benzene + oxygen study, ranging matrix composition through MR 10 : 1, 1 : 1, 1 : 60 (benzene : oxygen), was carried out to find optimum conditions for the appearance of the singlet–triplet spectrum. No absorption, other than that due to charge-transfer interaction, was observed with composition 1 : 60, even after many pulsed depositions. Experiments using composition 1 : 1 produced singlet–triplet spectra consistently. Relatively weak absorptions were observed in experiments with composition 10 : 1 after many pulsed depositions. Therefore three experiments with 1 : 1 compositions were generally performed on the remaining compounds. Pure benzene and toluene pulsed matrices did not show absorptions in the region of their evaluated singlet–triplet spectra.

Fig. 1(a), (b) and (c); 2(a), (b) and (c); 3(a), (b) and (c); 4(a), (b) and (c); 5(a) (b) and (c) show:

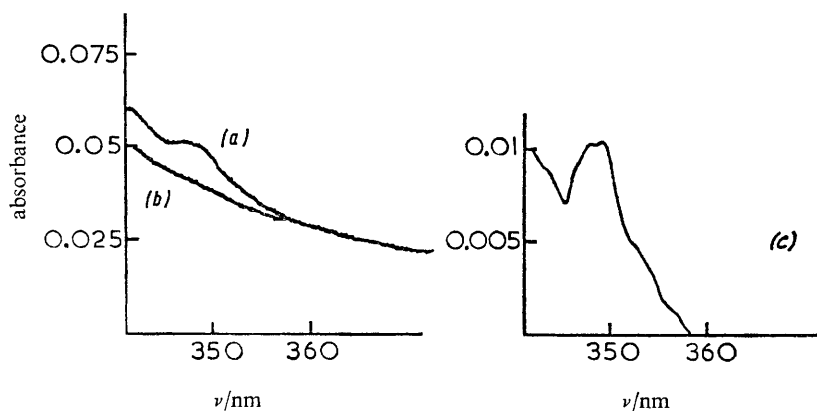(a) Typical absorption spectra of the aromatic compounds in an oxygen matrix

FIG. 4.—Singlet–triplet spectrum of *p*-fluorotoluene (PFT) at 10 K [see text for an explanation of the lettering (*a*), (*b*), (*c*)].
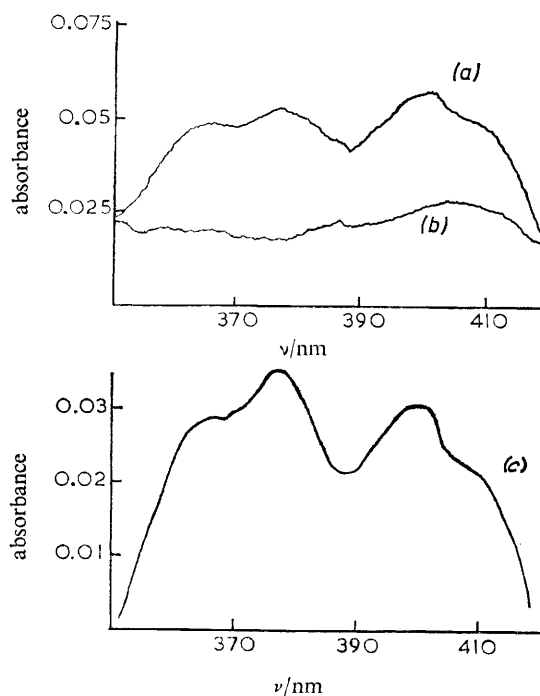
FIG. 5.—Singlet–triplet spectrum of styrene at 10 K [see text for an explanation of the lettering (*a*), (*b*), (*c*)].

after, typically, thirty pulsed depositions (M.R. 1 : 1), (*b*) the associated contact charge-transfer profiles obtained by normalising the measured charge-transfer absorption (typically after three pulses) to the actual number of pulses deposited (M.R. 1 : 1), (*c*) the evaluated singlet–triplet spectrum (M.R. 1 : 1).

The singlet–triplet absorption spectra of the following aromatic compounds were studied in oxygen matrices at 10 K : benzene, toluene, *para*-difluorobenzene (PDFB), *para*-fluorotoluene (PFT) and styrene. The results obtained are summarised in tables 1, 2 and 3.

TABLE 1.—OXYGEN PERTURBED SINGLET–TRIPLET SPECTRA FOR SOME SIMPLE AROMATIC COMPOUNDS (v/cm^{-1})

compound	v_{00}[a]	$v_{(1)}$	$v_{(2)}$	$v_{(3)}$	v_{max}
	29 410	30 395	31 350	32 260 [b]	
	29 500	30 500	31 300	32 200 [c]	
benzene	29 516	30 500	31 300	32 200 [d]	
	29 440	30 350	31 250	32 100 [e]	
	29 674	30 581	31 466	32 258 [f]	
	28 990	29 940	30 960	31 950 [b]	
toluene	28 800	—	—	—	30 800 [c]
	29 000 [g]	—	—	—	—
PDFB	28 800	—	—	—	29 850 [b]
	29 000	29 900	30 800	31 700 [c]	
PFT	28 330	—	—	—	28 800 [b]
	28 500	29 400	30 400	31 600 [c]	

[a] v_{00} taken at 40 % of v_{max} when no vibrational structure observed; [b] this work; [c] data from ref. (12); [d] data from ref. (4a); [e] data from ref. (3b); [f] data from ref. (2); [g] data from ref. (3c).

TABLE 2.—COMPARISON OF EXPERIMENTAL VAPOUR PHASE AND MATRIX FIRST SINGLET AND TRIPLET LEVELS FOR SOME SIMPLE AROMATIC COMPOUNDS

compound	S_1 energy $/cm^{-1}$	$/eV$	T_1 energy $/cm^{-1}$	$/eV$	$\Delta(S_1-T_1)$ $/cm^{-1}$
benzene	38 100	4.72	29 410	3.65	8690 [a]
	38 400 [b]	4.76	29 500	3.66	8900 [c]
toluene	37 200	4.61	28 990	3.59	8210 [a]
	37 200 [b]	4.61	28 800	3.57	8400 [c]
PDFB	36 770	4.56	28 000	3.47	8770 [a]
	36 800 [d]	4.56	29 000	3.60	7800 [c]
PFT	36 630	4.54	28 330	3.51	8300 [a]
	36 860 [d]	4.57	28 500	3.53	8360 [c]

[a] this work; [b] data from ref. (1); [c] data from ref. (12); [d] data from ref. (10b).

TABLE 3.—COMPARISON BETWEEN THE A BAND OF STYRENE IN VARIOUS PHASES AND ITS OXYGEN PERTURBED SINGLET–TRIPLET SPECTRUM

phase	$S_0 \rightarrow S_2$ $/nm$	$/cm^{-1}$	$S_0 \rightarrow T_1$ $/nm$	$/cm^{-1}$
vapour	238	42 020 [a]	—	—
perfluoromethyl-cyclohexane	240	41 670	390	25 600 [b]
oxygen matrix (MR 1 : 1)	243	41 150	396	25 250 [c]
			376	26 600
			361	27 700
argon matrix (MR 1 : 1200)	256	39 060 [c]		
	246	40 650		
	238	42 020		

[a] data from N. L. Allinger, J. C. Tai and T. W. Stuart, *Theor. Chim. Acta (Berl.)*, 1967, **8**, 101; [b] data from ref. (13); [c] data from ref. (27).

Corresponding paramagnetic bimolecular perturbation studies using nitric oxide as a matrix material at 10 K could not be carried out due to a strong absorption associated with the condensed gas in the spectral region of interest. The phenomenon has been noted by previous workers.[4a, 5]

Experiments performed in xenon heavy atom matrices show that singlet–triplet absorptions for all the compounds studied in oxygen matrices do not appear in the rare gas matrix with 1 : 1 composition.

DISCUSSION

COMPARISON BETWEEN THE OXYGEN HIGH PRESSURE AND MATRIX TECHNIQUES OF SINGLET–TRIPLET ENHANCEMENT

The results in tables 1 and 3 indicate that agreement between the perturbed singlet–triplet spectra obtained by the two techniques is good, with $<1\%$ difference in values for $\bar{\nu}_{max}$. Table 2 shows similar agreement for the energies of the lowest singlet and triplet levels for the substituted benzene compounds studied. Furthermore, pure benzene and toluene matrices and aryl+xenon matrices do not show absorptions in the spectral region of interest. The matrix technique has, however, the disadvantage that absolute extinction coefficients cannot be measured, as exact concentrations of substrate cannot be determined.

One prerequisite for compounds studied by the high pressure gas phase studies is a fairly high vapour pressure. Although this is an important factor in the matrix experiments it is less of a disadvantage. For example, it was found most convenient in this work to use 20 Torr of a 1 : 1 gas mixture, i.e. 10 Torr substrate in conjunction with the pulsed deposition technique. However, compounds with vapour pressures down to 5 Torr could have been used (utilising more pulsed depositions). Below 5 Torr careful, slow deposition or a larger pulsing volume in conjunction with a larger sample volume would probably prove effective.

Spectral shifts due to solute–solvent interactions are often encountered in the study of electronic transitions.[1, 18] Low molecular weight, saturated fluorocarbons have been used to minimise the effect and improve resolution.[13] However, aromatic compounds have limited solubilities in such media.[1] The only interaction in this work is that between the aromatic molecules and oxygen. The results may therefore be related to those found in the vapour phase.[12]

Evans' original report [3a] on the perturbation of singlet–triplet transitions in aromatic compounds by oxygen under high pressures mentioned that low temperature measurements, while experimentally difficult, might be of interest since vibrational structure would almost certainly be better resolved. A study of solid benzene+ oxygen mixtures at 4.2 K showed this to be substantially correct.[2] However, concentrations of oxygen $>2\%$ gave such highly scattering samples that absorption spectra were immeasurable. This is in obvious contrast to the optical transparency of the matrices formed in the present study. The results in tables 1 and 3 indicate the potential of the matrix technique as a supplement to vapour phase measurements. Progressions in the triplet state are never as well resolved as might be expected in any phase and an analysis of such data will be considered in the next section.

VIBRATIONAL PROGRESSIONS IN SINGLET–TRIPLET SPECTRA

The enhanced singlet–triplet absorption due to molecular species such as oxygen and nitric oxide is strongly associated with contact charge-transfer interactions.[19] The energy of the aromatic composite triplet state approximates to that of the

unperturbed aromatic triplet level. However, diffuseness is observed as a variety of geometric iosmers of the aryl+oxygen species are involved in the production of the overall absorption enhancement.[20] A red shift of ~ 40 cm^{-1} due to oxygen perturbation is predicted for pyrazine [21] which has been observed [3c] from the unperturbed [22] singlet–triplet spectrum. This collisional broadening can be accentuated by the Auger effect which accompanies the presence of oxygen. Thus, rapid deactivation of the higher vibrational levels to the zeroth level of the aromatic triplet state may occur.

As shown in fig. 1, 2 and 5, fairly well resolved vibrational structure may be obtained using the matrix technique and the following observations can be made regarding the benzene compounds listed in table 1.

(a) BENZENE

Analysis of the vibrational progression in the triplet state by the high pressure technique gives the following values: 900 ± 100 cm^{-1};[12] 885 ± 30 cm^{-1};[3a] 861 ± 50 cm^{-1};[2] 900 ± 100 cm^{-1}.[4a] The matrix technique affords the progression 950 ± 40 cm^{-1}. This indicates that, in general, greater precision in vibronic analysis is possible with the low temperature technique. The change in frequency of the v_1 mode of benzene on going from singlet to triplet manifolds has been estimated to be 25 cm^{-1}.[10a] Although the half-width of the benzene triplet structure is too broad to be definite at 10 K (440 ± 20 cm^{-1}), it appears that there is a real, but small, increase for the v_1 mode between the states (v_1 takes the value of 923 cm^{-1} in the first excited singlet state).[23]

(b) TOLUENE

Vibrational progression in the triplet state of toluene has not been observed before in its singlet–triplet absorption spectrum. It takes the value 985 ± 35 cm^{-1} in an oxygen matrix. This is an important result, since it clearly demonstrates an increase in frequency of the v_1 mode from its first excited singlet state value of 932 cm^{-1}.[24]

For substituted benzene compounds qualitative explanations of the variation of relative non-radiative rate constants as a function of excitation may be obtained if it is assumed that the singlet–triplet energy gap remains unchanged from the case of benzene, on which the analysis is based.[10] This is a good assumption for the aromatic compounds studied in this work, as will be discussed in the next section. Such rate constant data have not yet been reported for toluene. However, it has been suggested that low frequency C—F vibrations do not play a significant role as accepting modes for the available triplet state energy of disubstituted fluorobenzenes.[10b] Therefore, the presently determined optical mode frequency shift of $\sim +50$ cm^{-1} for toluene may be used to confirm one interpretation of the non-radiative rate constant data obtained by Phillips and Rockley [10b] on the fluorotoluenes. This observation also lends further experimental evidence to the theoretical treatment of such aromatic systems proposed by Heller, Freed and Gelbart.[10a]

(c) para-DIFLUOROBENZENE AND para-FLUOROTOLUENE

Although vibronic structure similar to that found in the vapour phase study [7] was not observed it is thought to be particularly difficult to make such assessments when dealing with absorbances <0.02. In other respects the positions of v (onset) and v (max.) are similar for corresponding experiments. It is interesting to note that the

para-fluorotoluene experiments required many pulsed depositions (typically 100 with 10 Torr pulsing pressures) before measurable spectra were obtained. This is more than twice as many as all other compounds studied and indicates that the transition is much weaker.

SINGLET–TRIPLET ENERGY GAP

As shown in table 2, the singlet–triplet energy gap for the aromatic compounds discussed above can be calculated as 8350 ± 450 cm^{-1} for the vapour phase study [12] and 8500 ± 275 cm^{-1} for the matrix study. The former value, along with the observation that the energy gap for the difluorinated compound was ~ 13 % less than that of benzene, led Rockley [25] to the conclusion that both *para*-fluorotoluene and *para*-difluorobenzene were true exceptions to the constancy of the value. However, the low temperature results indicate that for all compounds studied the energy gap is the same to within the experimental limit of the absorption band half-width. It is also within the limit of benzene data for earlier studies which take values of 8650 [3b] and 8200 cm^{-1}. [10a]

RELATIONSHIP BETWEEN THE A BAND OF STYRENE AND ITS
SINGLET–TRIPLET ABSORPTION SPECTRUM

Evidence for the suggestion by Salisbury [26] of a correlation in electronic configuration between the S_2 and T_1 levels of the styrenes has recently been presented. [13] In general, the S_2 (absorption maximum)–T_1 (onset value) energy gap has been found to be constant and equal to 2.45 ± 0.08 eV. The observation of a similar constancy for the S_2 (absorption maximum)–T_1 (absorption maximum) therefore allows accurate prediction of the triplet energy levels of many styrene derivatives in which no steric effects are present.

The A band vibrational structure is quite well resolved for styrene absorption in an argon matrix (MR 1 : 1200), [27] unlike the situation for solutions or glasses at 77 K. [28] The vibrational spacing take values of 1590 ($0 \rightarrow 1$) and 1370 cm^{-1} ($1 \rightarrow 2$). With so few members of the series we can say little about the anharmonicity, but the mean value of 1480 ± 160 cm^{-1} is little different from the ground state C==C stretching vibration (1632 cm^{-1}). [29] Similar resolution of the A band at $-130°$C (mixed alcohol solvent) of *trans*-stilbene gave values for the C==C stretching frequency of 1480 cm^{-1}. It should be noted, however, that this frequency seems to be very solvent sensitive. Thus frequency separations of ~ 1340 cm^{-1} are obtained in hexane, glycerol and perspex. [30]

As further indication of the similar electronic character of the S_2 and T_1 states of styrenes, the matrix oxygen perturbed S_0–T_1 spectrum of styrene shows vibration structure with a spacing of 1200 ± 170 cm^{-1}. This we assign to the C==C stretching frequency. The decrease in frequency of the vibration, as compared with the S_0 and S_2 states, is a result of a general loosening (decrease in bond order) of the olefinic double bond in the T_1 state.

XENON MATRIX EXPERIMENTS AT 10 K

As indicated above, the heavy atom perturbation of xenon does affect singlet–triplet processes in a low temperature matrix. [14] However, no enhancement of the singlet–triplet spectrum was observed for the aromatic compounds studied in this work. It may well reflect the fact that charge-transfer intermediates are necessary to lend intensity to singlet–triplet transitions even if the origin of the perturbation is solely magnetic. This is also indicated by the results of Grabowski [31] who computed

the extinction coefficients of singlet–triplet absorption for chloronaphthalene with various perturbing species. It was found that the relative effects of xenon : ethly iodide : oxygen were approximately in the ratios 1 : 10 : 100. It seems doubtful that the electronic structure of xenon would be favourable for participation in a charge-transfer mechanism, whereas evidence for such interaction has been presented in the case of halogenocarbon perturbing species.[32]

Future work could therefore well be directed towards the production of such halogenocarbon matrices at 10 K.

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