

STUDY OF DARK STATES IN NAPHTHALENE, PYRIMIDINE AND PYRAZINE BY DETECTION OF PHOSPHORESCENCE AFTER UV LASER EXCITATION

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The high-resolution fluorescence and phosphorescence detected spectra after excitation of the $(3a_g)^1$ and $(4a_g)^1$ vibronic states of the S_1 ($^1B_{3u}$) in naphthalene have been studied in a molecular beam. The residual Doppler linewidth of 20 MHz allowed rotational resolution. All lines were assigned and the rotational constants of the $(3a_g)^1$ and $(4a_g)^1$ states were determined. It has been shown that the intersystem crossing rates are independent of the rotational quantum numbers J and K up to $J=10$ in both excited vibronic states. The strong ISC rate of the $(4a_g)^1$ state is confirmed. No evidence was found for a promoting second triplet T_2 state. Detection of phosphorescence after excitation of the vibrationless S_1 ($^1B_{3u}$) state in pyrazine and the S_1 (1B_1) state in pyrimidine yielded no signal. This observation confirms the assumption that after excitation of the S_1 state the energy is transferred to high vibrational states of the S_0 state.

1. Introduction

In the theory of intramolecular radiationless transitions molecules are usually classified according to their behaviour under optical excitation as small, intermediate case or large molecules [1]. In a small molecule the excited state is coupled to only a few non-radiative, so called dark states. This results in an exponential decay with a quantum yield close to unity. In a large molecule on the other hand, the optical excited state is coupled to a dense manifold of dark background states, which acts as a quasi continuum. This opens an extra decay channel of the state, besides the radiative decay, to which the energy can flow. The decay will still be exponentially with a quantum yield less than unity. In the last years much attention has been paid to the intermediate case molecules. In such a molecule the optically excited state is coupled to a limited number of dark background states. The decay will in general be non-exponential, exhibiting quantum beats and/or biexponential decay, with quantum yields again smaller than unity.

This classification already indicates that most experiments in this field have been performed with pulsed laser systems, which allow a good resolution in the time domain, but a limited resolution in the

frequency domain. This especially implies that for large molecules an ensemble of rovibronic states rather than a single well defined state is excited. Consequently little is known about the rotational effects on the intramolecular radiationless decay. The important role rotations play in such decays has clearly been demonstrated in benzene by Riedle et al. [2]. High-resolution Doppler-free two photon spectroscopy showed that in the "channel three" region only $K'=0$ lines are present in the spectrum.

To elucidate the role of rotational effects on the intramolecular radiationless transitions we have studied in the present work the intersystem crossings with rotational resolution in pyrazine, pyrimidine and naphthalene by detecting the phosphorescence after excitation of the singlet S_1 state [3,4]. The molecules collide shortly after their optical excitation with a cooled surface. The resulting phosphorescence from the molecules, which are stuck on the surface is measured and compared to the directly detected fluorescence spectrum. By this method we were able to determine the relative intersystem crossing rates for each single rovibronic state.

Pyrazine serves together with pyrimidine as prototypes for the intermediate case molecule, and many data are available at the moment. For a recent review

we refer to ref. [5]. It has been demonstrated for pyrazine that the temporal decay of the first excited S_1 ($^1B_{3u}$) singlet state exhibits both quantum beats [6,7] and biexponential decay, which has shown to be magnetic field dependent [8,9]. These experimental findings have been interpreted in terms of a coupling between the first excited singlet state S_1 and nearly iso-energetic vibronically excited states of the lower lying triplet T_1 state. The vibrationless origin of the latter level is positioned 4056 cm^{-1} below the origin of the S_1 state. In a high-resolution experiment with a cw single frequency laser we have demonstrated the existence of the molecular eigenstates (MEs) [10]. It was found that each single rotational transition appears as a large number of lines (≈ 40). These MEs' spectrum can easily be deconvoluted into their zero-order singlet and triplet states in the case only one optical doorway state is present [11], a situation encountered for the $P(1)$ and $R(0)$ transitions. Recently we have also succeeded in a deconvolution of all $J'K'$ states up to $J' = 3$ [12]. It was found for rotational states up to $J' = 3$ neither the singlet-triplet coupling matrix elements nor the number of coupled triplet states systematically depend on the rotational quantum number J' . It appears however that the fluorescence intensities of the $K' = 0$ transitions are relatively weaker than the intensities of the $K' \neq 0$ transitions, which indicates a rotational effect on the intersystem crossing.

However, for a correct deconvolution procedure the absorption intensities should be used rather than the excitation intensities which are obtained in a laser-induced fluorescence experiment. Therefore we have recently studied [13] the absorption intensities of the individual MEs. This is done by observing the amount of laser energy which is absorbed by the molecular beam with the help of a bolometer detector [14]. These experiments clearly indicated that the quantum yield is a smoothly varying function over the different MEs within a single rotational transition, but decreasing with increasing J' . This qualitative result is in agreement with low-resolution measurements [15], which showed that the quantum yield (Y) can be written as $Y = 0.124 / (2J' + 1)$ for J' values in the range between 5 and 22. The conclusions derived from the bolometric detected spectra were based on the assumption that non or very little phosphorescence emerges from the excited state molecules. It was

shown, however, for other molecules that phosphorescence can occur after excitation of the singlet S_1 state. This has been demonstrated by Ito and co-workers [3,4] who detected the phosphorescence by the excited molecules after a collision with a surface. To clarify the situation for pyrazine we have applied the method of phosphorescence detection on this molecule.

Pyrimidine behaves very similar to pyrazine with as a main difference that the singlet-triplet gap in pyrimidine is of the order of 2000 cm^{-1} . As a consequence pyrimidine has a much less dense manifold of background states coupling to the S_1 state and therefore a smaller number of MEs, which simplifies the deconvolution procedure and analysis of the spectrum [16]. In pyrimidine it was also found that neither the singlet-triplet coupling matrix elements nor the number of coupled triplets show a systematic dependence on the rotational quantum numbers J' and K' [16]. The fluorescence lifetime on the other hand was found to be increasing with increasing K' , again pointing to a rotational effect on the intersystem crossing (ISC). For this reason we have also studied the phosphorescence spectrum of pyrimidine.

The fluorescence decay of single low lying vibronic states of the first excited S_1 ($^1B_{3u}$) singlet of naphthalene have been studied in a cell [17,18] and in a molecular jet [19]. All decays are single-exponential with a quantum yield of approximately 0.3 for the low vibrational states of S_1 . This quantum yield generally decreases with increasing vibrational excess energy. This places naphthalene in the category of large molecules as might be expected from the large singlet-triplet gap of over 10000 cm^{-1} in this molecule [20].

Howard and Schlag [21] measured the rotational dependence of the quantum yield for some selected vibronic states in naphthalene under cell conditions. A clear variation of the quantum yield over the rotational contour has been found. This result has been interpreted in terms of a spin-orbit coupling between the excited singlet S_1 state and the dense manifold of dark background states which originate from vibrationally excited T_1 states. The rotational dependence of the ISC rate in such a case is determined by the Franck-Condon weighted density of states; due to differences in rotational energies in both the S_1 and T_1 vibronic states the various rovibronic singlet states are coupled to different vibronic triplet states. Dif-

ferences in the Franck–Condon factors then account for the variations in ISC rates. In the case of nearly constant Franck–Condon weighted density of states over the measured energy range the ISC rate will be independent of the rotational quantum numbers.

High-resolution molecular beam spectra of the 0_0^0 and $(8b_{1g})_0^0$ vibronic bands of naphthalene have been measured previously with a resolution of 30 MHz [22]. This experiment clearly revealed the rotational substructure. All lines and intensities could be assigned in terms of an asymmetric rotor Hamiltonian with the appropriate intensities. Especially the well behaved intensity variations indicate that the ISC rate cannot be a strongly varying function of the rotational quantum numbers, at least in the 0^0 and $(8b_{1g})_0^0$ state of the S_1 electronic state. Furthermore the observation that all lines in the spectrum can be assigned, is in agreement with the large molecule limit.

The method of sensitized phosphorescence has been applied on the S_1 state of naphthalene with vibrational resolution by Ito et al. [4]. Their experiments demonstrated a strong vibrational dependence of the ISC rate: in general the ratio of phosphorescence to fluorescence intensities increases with increasing vibrational excess energy. Some vibronic states (e.g., the $(4a_g)^1$) showed a strongly enhanced ISC rate. This was interpreted to result from an accidental resonance with a vibronic state of the second triplet T_2 , which energy is expected to be close to that of the S_1 state. In the present work we have applied the phosphorescence method at rotational resolution to two vibronic states of naphthalene, the $(3a_g)^1$ and $(4a_g)^1$ vibrational states of S_1 , both with a vibrational excess energy of about 1400 cm^{-1} . The $S_1(3a_g)^1$ vibronic state was found to exhibit a normal ISC rate, while the $S_1(4a_g)^1$ vibronic state showed an enhanced ISC rate. In case such a strong ISC rate is due to an accidental resonance with a vibronic state of the second triplet state T_2 , it is expected to strongly affect the high resolution spectrum. For example molecular eigenstates can show up resulting from a coupling of the S_1 state and the sparse background of vibrational T_2 states. We have therefore focused our attention on this particular vibronic state.

2. Experimental

An extensive description of the molecular beam

apparatus and the laser system is already given elsewhere [22]. Therefore only the relevant features are given here. The experimental setup is schematically depicted in fig. 1. The molecular beam is formed by a continuous expansion of naphthalene (pyrimidine, pyrazine) seeded in argon through a nozzle with a diameter of $75\text{ }\mu\text{m}$. The backing pressure of argon was varied in the range of 0.25–1.5 bar. The samples of pyrazine and pyrimidine (Janssen Chimica, purity better than 99%) were kept at room temperature, while the sample of naphthalene (Riedel de Haen, purity 95%, and Janssen Chimica, better than 99%) was heated to 95°C , in order to achieve enough vapor pressure. All samples were used without further purification. The molecular beam was strongly collimated by two conical skimmers (diameter 1.5 mm) and pumped differentially.

At a distance of 30 cm from the nozzle the molecules were excited to the singlet S_1 state by the continuous wave radiation field of an intracavity frequency doubled ring dye laser (a modified Spectra Physics 380D). About 2 mW of single frequency UV radiation with a bandwidth of 3 MHz was obtained by using an angle tuned LiIO_3 crystal. For relative frequency measurements a part of the fundamental laser beam was sent through a sealed-off, temperature stabilized Fabry–Perot interferometer, while for absolute frequency calibration the absorption spectrum of iodine was recorded simultaneously. The total undispersed laser-induced fluorescence was collected by two spherical mirrors and imaged at the photocathode of a photomultiplier (EMI 9789 QA). Due to the low fluorescence quantum yield of the molecules under consideration here, a large fraction of the ab-

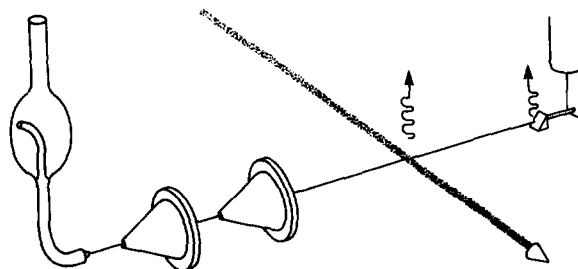


Fig. 1. Outline of the experimental setup. The molecular beam, formed from an expansion, is crossed by the laser. The beam collides with a cooled copper surface and the phosphorescence is detected.

sorbed energy will remain in the molecules in the beam. Depending on the nature of the coupling between the S_1 state and the background states the character of the state of the excited molecules in the beam will be either a high vibrational level of the triplet T_1 or T_2 state or of the singlet ground state S_0 , or even a mixture of the two cases. In the present experiment the excited state molecules travel over a distance of 30 cm (which corresponds to a time of approximately 0.5 ms) from the excitation region downstream to the phosphorescence detector [3]. The detector exists of a copper surface cooled to liquid nitrogen temperature and a 1 cm diameter quartz light pipe placed 1 cm above the cooled surface. The photons emitted from the surface are guided by this light pipe to a photomultiplier (EMI 9635 QA). After a few minutes, the cooled surface is covered with molecules from the sample.

After the collision with the surface the molecules in the beam are frozen to the surface and may release their surplus energy either by emission of a photon, or by transferring heat to the surface. If the molecule is in the triplet state, the collision can induce phosphorescence. However, if the excited state consists of high vibrational levels of the electronic ground state the most probable process would be the transfer of heat, due to the low Franck–Condon factors for emission. It is clear that therefore different detection methods can be used for the measurement of the internal energy of the molecule: for measuring the excited vibrational levels bolometer detection will be the most sensitive, while for the detection of molecules in the triplet state photon detection will give the best results. This indicates that these measurements give additional information: high phosphorescence signals indicate molecules in the triplet state. In the experiment performed here we have measured the total undispersed phosphorescence.

Because the laser excitation region and the phosphorescence detection region are separated with a diaphragm and since the large distance between these areas the amount of stray light from the laser as well as the light from the laser-induced fluorescence at the place of the phosphorescence detector are down by a factor of 10^4 by that in the excitation region. For most transitions involved we therefore can neglect contributions from stray laser light and LIF on the phosphorescence detector. During the experiment the

sensitivity of the phosphorescence detection varied slowly, probably due to the continuous deposition of molecules of the beam on the surface. Therefore all measurements have been performed several times. To eliminate the effects of changes in laser power and molecular beam, both the phosphorescence signal and the LIF signal were recorded simultaneously by a standard two-channel photon counting system (Ortec Brookdeal 5C1), interfaced with a PDP 11/23+ computer.

3. Results

3.1. Naphthalene

With the experimental setup described we have recorded simultaneously the laser-induced fluorescence spectrum (LIF) and the phosphorescence spectrum (SP) for two vibronic bands, the $(3a_g)_0^1$ and $(4a_g)_0^1$, of the S_1 ($^1B_{3u}$) \leftarrow S_0 (1A_g) electronic transition in naphthalene. Part of the naphthalene spectra are shown in fig. 2 (the $(3a_g)_0^1$ band) and in fig. 3 (the $(4a_g)_0^1$ band). The typical count rate of the spectrum of the $(3a_g)_0^1$ band is 50000 counts/s per mW laserpower for the LIF spectrum and 4000 counts/s per mW for the SP spectrum. For the $(4a_g)_0^1$ band these numbers are 3000 counts/s per mW (LIF spectrum) and 2000 counts/s per mW (SP spectrum). This clearly shows the vibrational dependence of the ratio I_F/I_P of the intensities of the LIF spectrum (I_F) and SP spectrum (I_P), which is in agreement with the low-resolution measurements [4]. The linewidths of the transitions of the LIF spectrum and SP spectrum were 12 and 20 MHz, respectively. In both cases the linewidth is dominated by the residual Doppler width due to the divergence of the molecular beam. Because of the spatial sensitivity of the collection optics for the LIF spectra, only a part of the fluorescence of the molecular beam is detected. This slightly narrows the linewidth. In the SP spectra however the complete molecular beam is detected.

In comparing the LIF and SP spectra, we notice that in the $(3a_g)_0^1$ vibronic band all lines are present both in fluorescence as in phosphorescence. We furthermore see that the relative intensities of the rotational lines in each spectrum are approximately the same. In the $(4a_g)_0^1$ vibronic band all lines which appear in

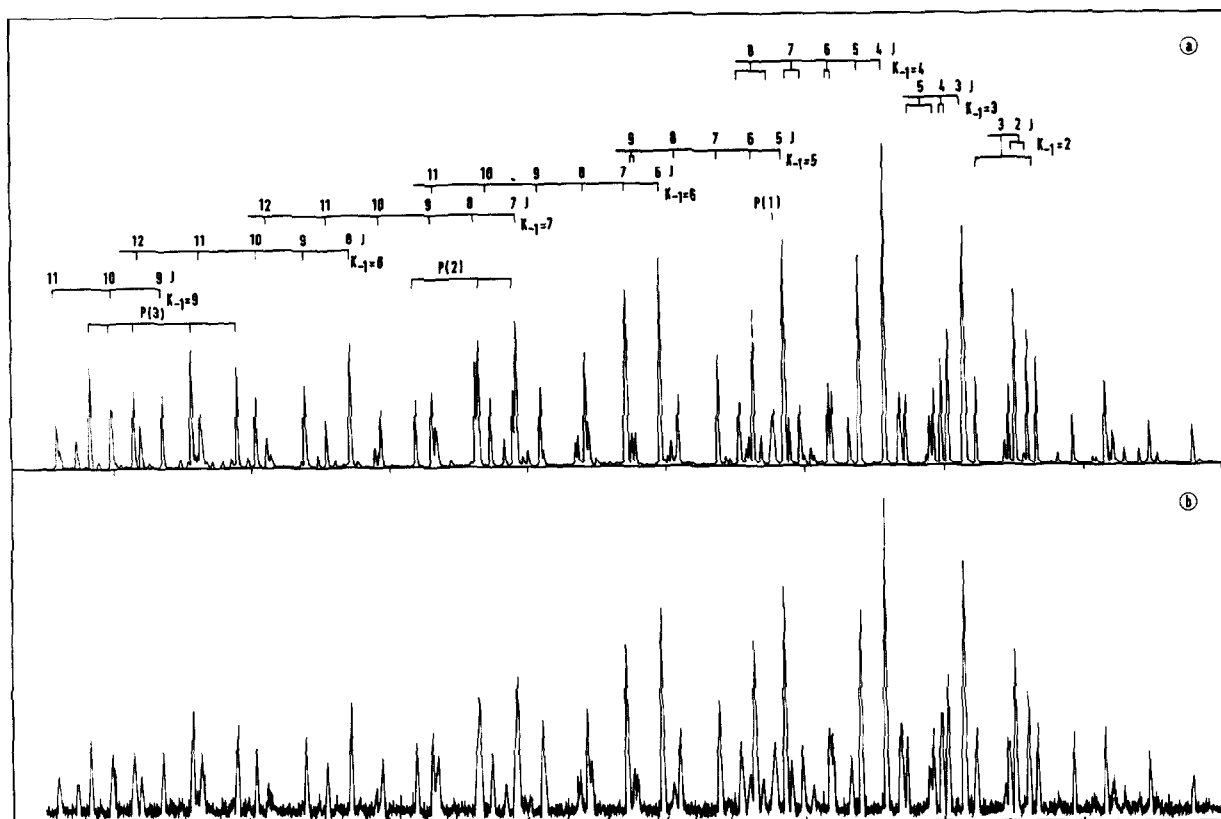


Fig. 2. High-resolution fluorescence (a) and phosphorescence detected (b) spectra of the Q-branch of the $(3a_g)_0^1$ electronic transition of naphthalene. The intensity axis is in arbitrary units. The frequency is increasing from left to right and marked every GHz.

the SP spectrum can also be identified in the LIF spectrum. However, some additional lines appear throughout the whole investigated frequency range in the LIF spectrum of the $(4a_g)_0^1$ band. These lines are not predicted by the asymmetric rotor calculation performed at the end of this section. We attribute these extra lines to either an isotopic species or a contamination in our naphthalene sample. Several potential candidates such as thianaphthene (C_8H_6S) have been investigated as a pure sample. We failed however to find a molecule which reproduced the extra transitions in the spectrum of the $(4a_g)_0^1$ band.

In order to investigate the rotational dependence of the ratio of intensities between the corresponding transitions in the SP and LIF spectra we have made a rotational assignment of the lines in the $(3a_g)_0^1$ and $(4a_g)_0^1$ bands. Such an assignment is furthermore needed to allow a search for possible extra splittings in the spectra due to ISC. For the $(3a_g)_0^1$ vibronic

band 200 lines in the central 30 GHz part of the LIF spectrum up to $J' = 12$ have been assigned. It turned out that it was possible to fit the observed transitions in the two bands with an asymmetric rotor Hamiltonian. The fit was made to a parallel a-type band, which confirms the symmetry of the vibration. All lines present in the spectrum could be identified. A least-squares fit of the experimental spectrum to the asymmetric rotor Hamiltonian yielded the rotational constants in both the ground and excited electronic state. The standard deviation of this fit was 2.5 MHz, well within the experimental linewidth. Table 1 lists the obtained molecular constants. The errors given are the standard deviation from the fit. The dominating source of errors, however, is the drift of the interferometer. An estimated uncertainty can be found by comparing the ground state rotational constants as obtained from different vibronic bands. A comparison between the present results for the ground state

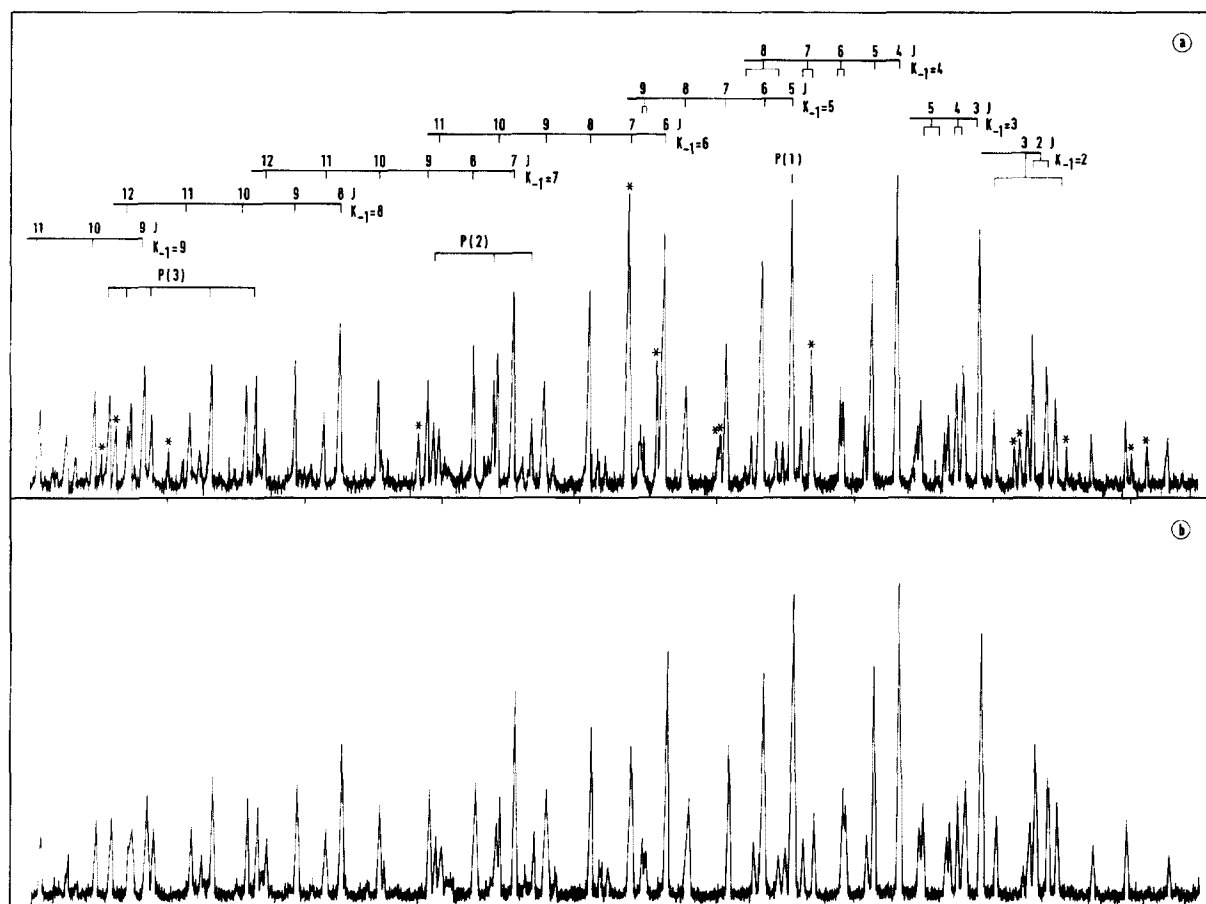


Fig. 3. High-resolution fluorescence (a) and phosphorescence detected (b) spectra of the Q-branch of the $(4a_g)^1$ electronic transition of naphthalene. The intensity axis is in arbitrary units. The frequency is increasing from left to right and marked every GHz. The lines marked with an asterisk only show up in the fluorescence spectrum.

Table 1

Molecular constants of the naphthalene molecule in the S_0 and the $(4a_g)^1$ and $(3a_g)^1$ vibronic states of the S_1 ($\Delta A = A' - A''$ etc.)

		$(4a_g)^1$	$(3a_g)^1$
S_0	A'' (MHz)	3117.6(5.7)	3113.6(2.7)
	B'' (MHz)	1231.7(0.2)	1230.7(0.2)
	C'' (MHz)	883.1(0.2)	882.3(0.2)
S_1	ΔA (MHz)	-81.35(0.05)	-78.06(0.03)
	ΔB (MHz)	-18.89(0.07)	-19.60(0.04)
	ΔC (MHz)	-16.59(0.05)	-16.31(0.04)
	ν_0 (cm^{-1})	33408.229(0.004)	33453.381(0.003)
	$\Delta\nu_0$ (cm^{-1})	1389.652(0.007)	1434.804(0.005)

constants and those from the 0_0^0 and $(8b_{1g})^1$ [22] bands shows that the uncertainties in the rotational constants are about five times the standard deviation.

The unperturbed relative intensities of the rotational lines in an a-type band are given by:

$$I = I_0 g_{J''K''_1K''_1} A_{J''K''_1K''_1} \times \exp[E(J'', K''_1, K''_1)/kT_{\text{rot}}], \quad (1)$$

where $A_{J''K''_1K''_1}$ are the Hönl-London factors, $g_{J''K''_1K''_1}$ are the statistical weights, $E(J'', K''_1, K''_1)$ is the energy of the electronic ground state and T_{rot} the effective rotational temperature of the molecules in the beam; k is the Boltzmann constant and I_0 the

normalized intensity. Since naphthalene is a near-prolate symmetric rotor we employ for $A_{J''K''L}K'$ the symmetric top expressions. The errors resulting from this approximation are negligible compared to the experimental inaccuracies in the intensity measurements. A fit of the experimental spectrum to eq. (1) yielded a rotational temperature of 4 ± 0.5 K.

We have assigned 220 lines of the central 40 GHz part of the SP spectrum of the $(4a_g)_0^1$ vibronic band with J' up to 12. Despite the slightly larger linewidth we preferred to analyze the SP spectrum because of the additional lines in the LIF spectrum. This band again corresponds to a parallel a-type transition, in agreement with the previous assignments. We performed a least-squares fit of the experimental spectrum to the asymmetric rotor Hamiltonian. The resulting rotational constants are given in table 1. The standard deviation of the fit was 7.5 MHz. The intensities were again fitted to eq. (1) yielding a rotational temperature $T_{\text{rot}} = 4.5 \pm 0.5$ K. The slightly higher rotational temperature for the $(4a_g)_0^1$ band as compared to the $(3a_g)_0^1$ band is due to a somewhat different argon backing pressure in the source.

With the help of the rotational assignments for the $(3a_g)_0^1$ and $(4a_g)_0^1$ band as discussed above we are now in the position to determine the ratio I_F/I_P for each individual rotational line in both bands. The most reliable result can be obtained using the Q-branch lines and P-branch lines with low J' values, because these lines are concentrated in a relative small frequency range. In this way the effect of changes in the sensitivity of the phosphorescence detector are minimized. Fig. 4 displays the ratios for J' values up to $J' = 10$ for both vibronic bands. In this figure each point for a given J' value corresponds to a different rotational line. It is clear from fig. 4 that the ratios are scattered randomly around an average value with J' and K' . We therefore conclude that the ratio I_F/I_P is independent of the rotational quantum numbers J' and K'_{-1} for J' up to 10.

3.2. Pyrazine and pyrimidine

We have furthermore investigated the LIF and SP spectra of the $0_0^0 S_1 (^1B_{3u}) \leftarrow S_0 (^1A_g)$ electronic transition in pyrazine and the $0_0^0 S_1 (^1B_1) \leftarrow S_0 (^1A_1)$ electronic transition in pyrimidine. In the case of pyrazine no SP signal was detectable, although the LIF

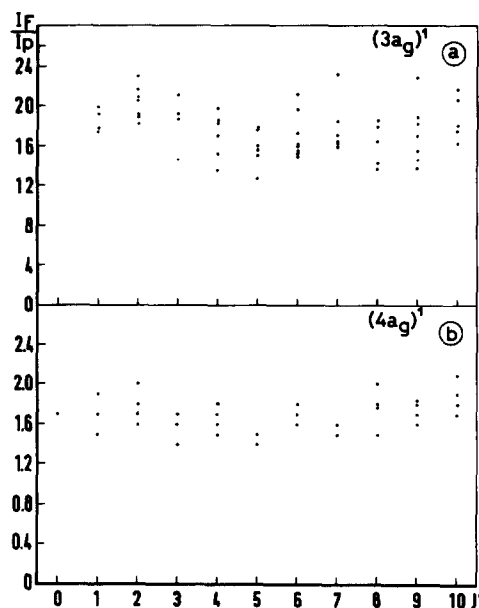


Fig. 4. The ratio I_F/I_P of the fluorescence intensity I_F and the phosphorescence intensity I_P as a function of the excited rotational state quantum number J' for the $(3a_g)^1$ state (a) and the $(4a_g)^1$ state (b). Different points correspond to different rotational lines.

signal on the strongest transitions amounts to 120000 counts/s per mW UV laserpower. This result is in agreement with the nearly complete absence of a sensitized phosphorescence signal for pyrazine as found by Goto et al. [23]. From the approximate average quantum yield of 0.01 of pyrazine for the low J' values [15], which is a factor 15 lower than that of the $(3a_g)^1$ vibronic state in naphthalene [19], we conclude that the energy contained in the beam of pyrazine molecules after laser excitation to the $S_1 (0^0)$ state is a factor of 40 higher than the energy contained in the beam of naphthalene molecules after excitation to the $S_1 (3a_g)^1$ state. If we further assume that the conversion efficiency for photon emission from the triplet state is the same in both molecules, it follows that the branching ratio for a radiationless decay of the $S_1 (0^0)$ state of pyrazine to highly excited vibrational states of the singlet electronic ground state is at least a factor of 200 higher than to the background triplet states. As a minimum detection limit a signal-to-noise ratio of three has been assumed.

For pyrimidine a weak signal with a countrate of 150 counts/s per mW UV laserpower (signal-to-noise

ratio 1) has been obtained on the phosphorescence detector. This was for the strongest fluorescence lines, where the LIF intensity was 800000 counts/s per mW UV laserpower. This signal on the photomultiplier of the SP detector is approximately the same as the estimated signal from the LIF, which mirrors by the copper surface of the SP detector onto its photomultiplier. It was therefore concluded that again for pyrimidine no SP signal is detectable. From an approximate quantum yield of 0.4 [24], and with the same assumptions made above for pyrazine we calculate that in the S_1 (0^0) state of pyrimidine the branching ratio for radiationless decay of the S_1 (0^0) to the S_0 state is at least a factor of 100 higher than to the T_1 state.

4. Discussion

The ratio of the phosphorescence signal I_P to the fluorescence signal I_F can be expressed as

$$\frac{I_P}{I_F} = A \frac{k_{nr}(S_1 \rightarrow T)}{k_r(S_1 \rightarrow S_0)} \times \exp\{-[k_r(T \rightarrow S_0) + k_{nr}(T)]\tau\} Q. \quad (2)$$

In this equation A governs all experimental effects such as collection efficiency, photomultiplier sensitivity etc. Here $k_r(S_1 \rightarrow S_0)$ and $k_{nr}(S_1 \rightarrow T)$ represent the radiative decay rate and the nonradiative ISC rate of the singlet S_1 state, respectively. Further $k_r(T \rightarrow S_0)$ and $k_{nr}(T)$ are the radiative decay rate of the triplet state T to the S_0 electronic ground state and the total nonradiative decay rate of the triplet state, respectively. In the case that $k_r(S_1 \rightarrow S_0)$ is much smaller than $k_{nr}(S_1 \rightarrow T)$ and the internal conversion rate $k_{nr}(S_1 \rightarrow S_0)$ is negligible, the ratio $k_{nr}(S_1 \rightarrow T)/k_r(S_1 \rightarrow S_0)$ is equal to the inverse of the quantum yield. The exponential factor describes the decrease in the number of molecules in the excited triplet state during the travel time τ (in our case 0.5 ms) between laser excitation and the collision on the copper surface. This decrease takes place either through phosphorescence (the radiative decay rate $k_r(T \rightarrow S_0)$) or through ISC to high vibrational states of the singlet ground state $k_{nr}(T \rightarrow S_0)$. The factor Q gives the efficiency of emitting a photon by a molecule in the triplet state after it hits the copper surface. This factor is assumed to be independent of the rotational quantum numbers.

It is reasonable to assume that the factor Q in pyrazine and naphthalene will be of the same order of magnitude. Hence the absence of any phosphorescence signal detected in pyrazine is either due to a small value of $k_{nr}(S_1 \rightarrow T)/k_r(S_1 \rightarrow S_0)$ or to a large total triplet decay rate in this molecule. Since the fluorescence quantum yield of pyrazine is 0.01 it follows that a large triplet decay is responsible for the lack of phosphorescence signal. The oscillator strength of the $T_1 \leftarrow S_0$ transition is known to be very small. Therefore the radiative decay of the molecules in the excited triplet state in the travel time τ will be negligible. The combination of a strong signal with a bolometer detector [13] and an absence of signal with a phosphorescence detector leads to the conclusion that the electronic excitation energy of the S_1 state pyrazine is converted to highly excited vibrational states of the singlet ground state.

This conclusion is in agreement with previous studies on pyrazine, where the decay rates of triplet states near the S_1 origin were found to be $3 \times 10^6 \text{ s}^{-1}$ [25]. This fast decay rate can be ascribed to a strong $T-S_0$ ISC. It was found furthermore from a deconvolution procedure of the MEs of pyrazine that the zero-order triplet states have decay rates on the average of $2 \times 10^6 \text{ s}^{-1}$ [26]. The present results confirm that the T_1 triplet background states are strongly coupled to the highly vibrational excited states S_0^* of the singlet ground state. The first excited singlet state transfers its energy on a timescale which is short compared to 1 ms to vibrational energy of the singlet ground state either directly ($S_1 \rightarrow S_0^*$) or via the triplet channel ($S_1 \rightarrow T_1 \rightarrow S_0^*$). The model proposed by Amirav in which the S_1 state couples to a small number of T_1 states which in turn are coupled by internal conversion to a high background of triplet states is in contradiction with the combined results of the present phosphorescence and bolometer experiments.

In pyrimidine the situation is very similar to that in pyrazine. There too is found that the triplet decay rates are in the order of $2 \times 10^6 \text{ s}^{-1}$ [25]. We conclude that the electronic excitation energy of the S_1 state in pyrimidine is also converted into vibrational energy of the singlet ground state.

For naphthalene it was shown that the ratio of the phosphorescence signal to the fluorescence signal is constant for each rotational J' , K' state up to $J' = 10$. Because the singlet radiative decay rate is independent of the rotational quantum numbers, this means

that the ratio I_P/I_F directly reflects the ISC rate $k_{nr}(S_1 \rightarrow T)$. This is under the reasonable assumption that the dependence of the triplet decay rate on J' is negligible. We therefore conclude that the ISC in naphthalene for the vibronic states investigated in the present work is independent of the rotational quantum numbers. This is consistent with the case of a spin-orbit coupling of the excited singlet state to a very dense manifold of triplet states. With the formula of Haarhoff [27] and a S_1 -T energy gap of 12000 cm^{-1} a triplet background density of $10^{10}/\text{cm}^{-1}$ is calculated. It is therefore reasonable to assume that the density of background states is uniform over the energy range we are probing, which indeed results in a rotational independent decay rate in accord with the observation. A rotational independent ISC rate was found in benzene too by Schubert et al. [28]. The temporal decay of some selected rotational states was shown to be independent of the rotational quantum numbers. The constant ISC rate appears to be typical for a large molecule as benzene and naphthalene.

Special attention should be paid to the $(4a_g)^1$ vibronic state of naphthalene. All lines in our high-resolution SP spectrum could be assigned with the appropriate relative intensities. Furthermore an ISC rate independent of J' has been found. These observations make an enhanced ISC with the sparse manifold of a nearly degenerate second triplet state T_2 highly improbable. In the case of a strong S_1 - T_2 ISC extra splittings of the rotational lines are expected while due to the difference in rotational energy in the S_1 and the T_2 state a strong rotational dependence of the ISC rate is to be expected. Neither of the two effects have been observed in the present work. This indicates the absence of a strong ISC between the S_1 and T_2 state.

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