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(24 January - 25 March 1983)

ENERGY CONVERSION IN VAN DER WAALS COMPLEXES OF s-TETRAZINE AND ARGON

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In press: Faraday Disc. Chem. Soc. (1983).

Energy Conversion in Van der Waals Complexes of s-Tetrazine and Argon

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Received 17th January, 1983

ABSTRACT

The van der Waals complex T.Ar has been prepared by expanding argon seeded with s-tetrazine through a nozzle. The complex dissociates when excited to single vibronic levels of the $S_1(^1B_{3u})$ state of tetrazine. Information about both the vibrational state distribution of the dissociation fragment T and vibrational relaxation which takes place in the complex has been obtained from spectrally resolved and time-resolved fluorescence.

The relative yields of relaxation and dissociation processes depend upon the excess vibrational energy ε_w absorbed by the van der Waals modes. The magnitude of ε_w was varied using different sequence transitions of the van der Waals modes, by tuning the laser successively to different wavelengths within the contour of a particular absorption band. The observed effects can be interpreted qualitatively in terms of the momentum gap law.

The dissociation of the $\overline{6a^1}$ state of T.Ar proceeds via two consecutive steps. Lower and upper limits to the dissociation energy D_0' (of the $\overline{6a^1}$ state) are 276 cm^{-1} and 448 cm^{-1}. Energy transfer from the 16a mode as well as from the 16b mode to the van der Waals bond gives rise to dissociation of the complex. The dissociation rates are in the order of $10^9 s^{-1}$ and they are dependent on ε_w.

1. INTRODUCTION

Van der Waals complexes are suitable prototype systems for studies of photodissociation and vibrational redistribution in polyatomic molecules. Generally, the dissociation energy D_0' of a van der Waals bond is smaller than a quantum of a molecular vibration, and therefore excitation of a single vibronic level of a molecule which is part of a weakly bound complex will eventually cause rupture of the van der Waals bond. The rate of the vibrational energy transfer process within the complex, giving rise to dissociation of the complex, competes with other deactivation processes of the electronically excited complex. Experiments in which the supersonic expansion technique is combined with sophisticated spectroscopic techniques have given interesting results[1]. The results of such studies have initiated extensive theoretical work[2].

Spectroscopic studies of vibrational predissociation and vibrational relaxation of vibronically excited complexes of s-tetrazine and argon have been reported in references 3 and 4. The spectra showed three different kinds of emission bands: (i) resonance emission from the originally excited level of the complex, (ii) emission bands originating from vibronic levels of the complex populated by intramolecular vibrational energy flow within the complex, which might be collision-induced, and (iii) emission from dissociation products. The torsional mode 16a appeared to be particularly important in the vibrational predissociation process. The observed emission spectra and the decay times of selectively detected emission bands give rise to the conclusion that one quantum of mode 16a is transferred to the van der Waals bond thus causing dissociation of the complex. No other modes than 16a were found to be directly involved in the dissociation process.

In the present study we will show that the energy of one quantum of the 16a mode is not enough to cause dissociation of the complex. This implies that energy transfer of one 16a quantum can only give rise to rupture of the van der Waals bond if the initial state contains already a sufficient amount of vibrational energy in the van der Waals modes. The dissociation process is schematically represented by arrow a in fig. 1 and the vibrational redistribution process is represented by arrow b. The redistribution process might be induced by collisions. In this paper we will examine the effect of collisions and the influence of excess vibrational energy stored in the van der Waals modes on the processes displayed in fig. 1.

Detailed information about fluorescence and absorption spectra of tetrazine vapour and tetrazine-argon van der Waals complexes is available in the literature [5,6]. A schematic representation of some normal modes of tetrazine, according to ref. 7, is given in fig. 2. Only modes with relatively low frequencies have been represented; the frequencies in the ground state and the excited electronic state are given in table 1. Levy and collaborators[6] have reported high resolution spectroscopic studies of s-tetrazine (T) and the van der Waals complexes T.X and T.X_2 (X= He, Ar or H_2). The structure of the spectra is consistent with a geometry in which X is situated on the out-of-plane C_2 axis of tetrazine. For the complexes T.X_2 the spectral shifts (with respect to the corresponding transitions of T) are twice as large as for T.X. This indicates that the X species are occupying equivalent positions. Throughout this paper we will denote vibronic levels and transitions in the complex T.Ar with a line on top of the assignment (e.g. $\overline{6a_0^1}$ denotes a transition in T.Ar).

2. EXPERIMENTAL

The complexes T.Ar and T.Ar_2 were produced in a supersonic expansion of argon seeded with approximately 0.03% of s-tetrazine. The carrier gas was conducted through a steel bottle containing s-tetrazine at a temperature of $(18\pm1)^0$C. A free yet was formed by expansion of the gas through a 0.050 mm pinhole into a chamber pumped by a Roots pump (350 m^3/h) backed by a mechanical forepump (25m^3/h). The stagnation pressure of the gas was varied between 1 and 1.6 bar. The continuous jet was crossed by a focused laser beam at a distance z downstream of the nozzle. The diameter of the laser beam was approximately 0.03 mm in the central part of the jet. In our experiments z was changed between 0.03 and 1.5 mm by moving the nozzle with respect to the laser beam which was fixed in space. The dimensions of the observed area were taken as small as possible (i.e. $\leq$ 0.1 mm x 1.0 mm depending on z) in order to avoid detection of fluorescence emission from molecules outside the jet.

Optical excitation of the van der Waals molecules was achieved with a dye laser synchronously pumped by an argon-ion laser. The bandwidth of the exciting light was 0.1 or 0.2 or 1.0 cm^{-1}. Time-resolved measurements of the fluorescence were carried out with picosecond pulses ($\tau_p \approx$ 7 ps or 80 ps) from the mode-locked laser system. The fluorescence emission was dispersed with a 1.5 m Jobin Yvon monochromator THR 1500 (0.24 nm/mm) equipped with two exit slits in order to allow either spectrally resolved or time-resolved measurements. In most of the experiments the spectral bandwidth of the detection system was 10 cm^{-1}, sometimes it was 15 cm^{-1}. Before and after each experiment a calibration of the wavelengths and the linewidth of the dye laser was performed with an accuracy of $\pm$ 1 pm (i.e. $\approx$ 0.03 cm^{-1}).

Fluorescence spectra were measured using a cooled magnetically defocused EMI 9558 QA photomultiplier. For the time-resolved measurements a Philips XP 2020 photomultiplier or a Varian Cross-field VPM 154 M was used. The photomultiplier is attached either to a Photon Counting System or to a Single Photon Counting system. The time resolution of the detection system is better than 100 ps.

Peak positions of emission bands could be obtained with an estimated accuracy between ± 1.5 cm^{-1} and ± 2 cm^{-1} depending on the intensity of the emission band. The estimated error in the peak positions of the excitation bands is less than ± 1 cm^{-1} except for very weak bands.

Before each series of experiments s-tetrazine was destilled into a steel bottle which forms part of the gas supply line to the nozzle. s-Tetrazine was synthesized according to the method of Spencer, Cross and Wiberg[7] . After the last step of the preparation s-tetrazine is sublimated several times by means of a freeze and thaw cycle in order to get rid of volatile impurities. The end product is stored in the dark under vacuum at -20°C.

3. RESULTS AND DISCUSSION

a. Spectroscopic observations.

Fig. 3 shows the $\overline{0_0^0}$ band of the fluorescence excitation spectrum of T.Ar. This spectrum exhibits also the molecular 0_0^0 band which appears as an extremely weak feature 23 cm^{-1} to the blue of the $\overline{0_0^0}$ band. Three stronger bands appear at +34, +38 and +43 cm^{-1} from the $\overline{0_0^0}$ band. These bands must be ascribed to the complex because their relative intensities with respect to the $\overline{0_0^0}$ band are independent of the experimental conditions. The band at +43 cm^{-1} which exhibits the same spectral structure as the $\overline{0_0^0}$ band, is ascribed to the $\overline{\sigma_0^1}$ transition, i.e. the transition v"= 0 → v'= 1 of the (totally symmetric) van der Waals mode σ. The bands at +34 and +38 cm^{-1} are probably due to transitions in which the (non-totally symmetric) bending modes β_y and β_z are involved. In the emission spectrum of T.Ar, observed after $\overline{0_0^0}$ excitation, again three weak bands are present. They appear at positions -33, -37 and -41.5 cm^{-1} from the $\overline{0_0^0}$ band.

The relative intensities of both the $\overline{\sigma_0^1}$ absorption band and the $\overline{\sigma_1^0}$ emission band, with respect to the intensity of the parent band $\overline{0_0^0}$ are approximately 0.02. The low Franck Condon factors indicate that electronic excitation of the complex causes a very small change of the equilibrium distance T-Ar, while the lower part of the intermolecular potential is only slightly changed.

It is not clear why the spectra should exhibit $\overline{\beta_0^1}$ and $\overline{\beta_1^0}$ transitions of the nontotally symmetric bending modes. Perhaps the corresponding bands must be ascribed to transitions $\overline{\beta_0^2}$ and $\overline{\beta_2^0}$.

The zero-point-level fluorescence spectrum of T.Ar is red-shifted 23 ± 1.5 cm^{-1} with respect to the 0^0 fluorescence spectrum of the free tetrazine molecule. Apparently, the intermolecular potential well is 23 cm^{-1} deeper in the excited electronic state than in the ground state. The vibrational structure of both spectra is identical. The main emission bands are $16b^0_2$, $16a^0_2$, $6a^0_1$, $8a^0_1$ and several 6a progressions of these bands. The spectral shifts of the bands are (−23 ± 1.5) cm^{-1} except for the $\overline{16b^0_2}$ band which is shifted (−18 ± 1.5) cm^{-1} with respect to the $16b^0_2$ band in the spectrum of the free tetrazine molecule. Table 2 shows the frequencies of some bands in the fluorescence excitation spectrum of T.Ar, including the weak hot band $\overline{16b^1_1}$. The frequencies (ν_{vac}) are referring to the peak positions of the excitation bands. In these experiments the emission was always detected in a resonance band , for instance, the excitation bands $\overline{0^0_0}$ and $\overline{6a^1_0}$ were measured by detecting the $\overline{6a^0_1}$ and $\overline{6a^1_2}$ emission bands respectively. The spectral shifts of the excitation bands(with respect to the corresponding bands in the spectrum of the uncomplexed molecule)are not identical. This indicates that the depth of the intermolecular potential is slightly affected by the vibrational motion of the nuclei of the tetrazine molecule. This effect seems to be more pronounced in the excited electronic state than in the ground state.

The fluorescence excitation bands all display the same spectral structure (cf. Fig. 3). This structure has not yet been analysed. The band contour is a superposition of rotational structure and sequence band structure of activated Van der Waals modes. The contribution of such sequence transitions v" → v' with $\Delta v = 0$ to the band contour is indicated by the following experiment. When the laser frequency is tuned successively to different positions within the excitation band, the spectral positions of the resonance emission bands shift in the same way. As an example, Table 3 gives the positions of the main emission bands of the complex (center of the band) for three different frequencies (excitation bandwidth 0.1 cm^{-1}) within the $\overline{6a^1_0}$ excitation band. The shifts observed for the intense resonance emission band $\overline{6a^1_2}$ equal those of the excitation frequency. Within the experimental error this is also the case for the much weaker resonance emission band $\overline{6a^1_0 16a^0_2}$. On the other hand, the shifts observed for the emission bands $\overline{16a^2_2}$ and $\overline{5^1_1}$, which originate from a relaxed level of the complex, are smaller, but they both show an increasing blue shift. This behaviour is also exhibited by the weaker relaxed emission bands of the T.Ar complex (not presented in Table 3). The observations are plausible when the formation of the van der Waals complexes in the supersonic jet is considered. These species are formed by three-body collisions, the third particle is required for the stabilization of the complex. In a supersonic expansion equilibration of translational and rotational degrees of freedom is more efficient than the equilibration between vibrational and translational degrees of freedom. For this reason it is concluded that in the electronic ground state of the complex several levels of the Van der Waals modes are populated.

Fig. 4 displays a schematic representation of a Morse type intermolecular potential as a function of the distance between the argon atom and the molecular plane of $^1B_{3u}$ s-tetrazine for some molecular vibronic states. For each of these curves the vibrational levels of the van der Waals stretching mode are shown. When the laser frequency is tuned into the blue wing of the excitation band, levels v' > 0 of the van der Waals vibration are excited via sequence transitions v" → v' with $\Delta v = 0$. This is due to the fact that the frequency of the van der Waals vibration in the excited electronic state is higher than in the ground state; the shapes of the potential curves are probably very similar in both electronic states. Resonance emission bands should exhibit the same spectral shift as the excitation frequency. The observation that emission bands originating from relaxed levels of the complex show a smaller shift than the excitation frequency can be considered as an indication that the vibrational energy transfer within the complex is collision-induced, so that energy relaxation takes place.

A lower limit to the intermolecular well depth can be deduced from the observation of the $\overline{16b}^1_1$ excitation band. This weak band could be observed at distances from the nozzle up to 1.5 mm which implies that the complex T.Ar in its vibrational state $\overline{16b}_1$ exists at least 1 μs after it was formed. Since vibrational predissociation times of T.Ar appear to be shorter than 1 ns (section 3b), the appearance of the $\overline{16b}^1_1$ excitation band at distances relatively far downstream of the nozzle indicates that the magnitude of the 16b quantum is too small to break the Van der Waals bond. Therefore a lower limit to the dissociation energy D_0'' in the electronic ground state is 254 cm^{-1} for the vibrational level $\overline{16b}_1$. If it is assumed that D_0'' is independent of the molecular vibrations in the electronic ground state, a lower limit of 254 + 23 = 277 cm^{-1} for D_0' in the vibrationless ${}^1B_{3u}$ state follows from table 2. An upper limit to D_0' follows from the observation that excitation of the $\overline{6a}^1$ level always gives rise to dissociation of the complex. In these experiments the dissociation fragment tetrazine is formed in the $16a^1$ vibronic state (not in the 0^0 state). This result is independent of the position of the excitation frequency within the $\overline{6a}^1_0$ band. Therefore the upper limit to D_0' is 703-255 = 448 cm^{-1} for the $\overline{6a}^1$ state of the complex.

This value is probably too high since the dissociation fragment tetrazine appears to be rotationally excited (see fig. 5). For this reason, the calculated value of 448 cm^{-1} must be reduced with the rotational energy gained by the tetrazine molecule. However, it should be noted that such a calculation is not reliable when the energy of the initial state is not known with certainty. We attribute the appearance of rotational energy in the liberated tetrazine molecule, at least in part, to the population of levels $v_\sigma > 0$ by optical excitation of the van der Waals stretching vibration in the $\overline{6a}^1$ state. More experiments have to be done in order to elucidate this point.

The observed difference between the frequencies of the van der Waals stretching mode in ground and excited electronic state is approximately 1.5 cm^{-1}. This value is in agreement with the observed difference of 23 cm^{-1} between the potential well depths if we assume Morse potentials with the same steepness parameter for both electronic states and a value of D_0 between, say, 275 and 450 cm^{-1}.

b. Vibrational relaxation and dissociation.

In ref. 4 we have reported the preliminary results of time-resolved experiments dealing with the decay of selectively detected emission bands in the dispersed fluorescence, observed after excitation of the $\overline{6a}^1$ level of T.Ar. The main bands in this spectrum originate from the prepared level $\overline{6a}^1$, from the relaxed levels $\overline{16a}^2$, $\overline{16a^1 16b^1}$ and $\overline{5}^1$, and from the $16a^1$ level of the tetrazine molecule which is formed by dissociation of the complex. The decay times of these levels were obtained from the slope of a semilogarithmic plot of the fluorescence intensity versus time.

An indication of the processes which take place after excitation of the $\overline{6a}^1$ level was obtained from a comparison of these decay times with those observed after direct excitation of the corresponding states of tetrazine in a supersonic jet. These latter decay times are almost identical with those measured in the static gas phase at room temperature. It turned out that the decay times of the relaxed levels $\overline{16a^2}$ and $\overline{16a^1 16b^1}$ of T.Ar are significantly shorter than those measured for tetrazine. On the other hand, the decay times of the levels $\overline{6a}$ and $\overline{6^1}$ of T.Ar and $16a^1$ of the liberated tetrazine appeared to be identical with those measured directly for tetrazine in the gas phase or in a supersonic jet. From these observations it was concluded that the vibrational predissociation of the $\overline{6a^1}$ state proceeds via two consecutive processes: firstly, a vibrational relaxation process $\overline{6a^1} \rightarrow \overline{16a^2}$ or $\overline{6a^1} \rightarrow \overline{16a^1 16b^1}$, which has no significant effect on the lifetime of the optically prepared state $\overline{6a^1}$, and secondly, the actual dissociation process which is fast enough to cause a significant reduction of the lifetime of the $\overline{16a^2}$ and $\overline{16a^1 16b^1}$ states of the complex. Since no emission from tetrazine in the vibrationless state 0^0 was observed, it was concluded that one quantum of the torsional vibration 16a is transferred from tetrazine to the van der Waalsbond giving rise to the ejection of the argon atom.

This conclusion is supported by the results obtained after excitation of the $\overline{16a^2}$ level of T.Ar. The main emission bands originate from the prepared level $\overline{16a^2}$ and from the $16a^1$ level of the dissociation fragment. Once again, the lifetime of the $\overline{16a^2}$ level appeared to be reduced with respect to the lifetime of the $16a^2$ level of uncomplexed tetrazine.

According to this interpretation of the preliminary data presented in ref. 4 an important dissociation channel of vibronically excited T.Ar is based on the transfer of one quantum of mode 16a to the van der Waals vibrations, probably the stretching mode. It has to be noted that the 16a quantum (255 cm^{-1}) is smaller than the lower limit to the dissociation energy D_0' which is 277 cm^{-1} for the $\overline{0^0}$ state and (according to table 2) 278 - 15 = 263 cm^{-1} for the $\overline{16a^2}$ state. Therefore it must be concluded that after the vibrational relaxation process $\overline{6a^1} \rightarrow \overline{16a^2}$ which might be collision-induced, has taken place, the excess vibrational energy stored in the van der Waals modes exeeds the energy difference $D_0' - 255$ cm^{-1}. The observation that optical excitation of $\overline{16a^2}$ can give rise to the dissociation process $\overline{16a^2} \rightarrow 16a^1 + Ar$ implies that in these experiments a sufficient amount of energy is absorbed by the van der Waals modes (as a result of sequence transitions $v'' \rightarrow v'$ with $\Delta v = 0$) to compensate for the energy deficiency $D_0' - 255$ cm^{-1}.

In the present paper we will pay attention to: (i) the role played by collisions between the van der Waals complexes and the atoms of the expanding carrier gas, and (ii) to the effect of optical excitation of van der Waals vibrations on the yields of relaxation and dissociation processes. The results of improved time-resolved measurements will be considered.

In order to obtain information about the influence of collisions we have varied the distance z between the illuminated part of the jet and the nozzle. The collision frequency and the collision energy decrease strongly with increasing z. The energy absorbed by van der Waals vibrations has been varied by using different excitation frequencies ν_{exc} within a particular absorption band. When ν_{exc} is shifted to the blue the complex ends up in higher levels of the van der Waals modes in the excited electronic state (cf. section 3a).

In our experiments collision - induced vibrational relaxation of uncomplexed tetrazine is negligible (i.e. the intensity of relaxed emission bands is less than 0.5% of the intensity of resonance emission). This means that the distribution of vibronic states of tetrazine formed in the dissociation reaction is not disturbed by collisions in the jet. However, under the same experimental conditions collisional effects may not be negligible for van der Waals complexes, even for large values of z. This is because the hard sphere cross section of the complexes is greater than that of uncomplexed tetrazine and especially, because the density of vibrational states of the complex is considerably higher than that of the free molecule, due to the contribution of the van der Waals vibrational manifolds. For these reasons it is inevitable that vibrational relaxation of the complexes is influenced by collisions in the jet. If the density of the background levels, due to the contribution of stretching and bending modes, is sufficiently high, vibrational energy flow will occur in an isolated complex, but generally the efficiency of this process will be enhanced by collisions.

Fig. 6 shows a part of the fluorescence spectrum obtained after excitation of the $\overline{6a^1_0}$ band at 18808.8 cm^{-1} (frequencies are given as ν_{vac}, wavelengths are presented as λ_{air}). When the excitation is achieved at 18808.8 cm^{-1} the complex ends up in the lowest vibrational level(or in the lower levels) of the intermolecular potential well (cf. section 3a). It depends on the width of the rotational contours of adjacent sequence bands of the van der Waals modes whether the excitation process gives rise to the population of single levels of the van der Waals vibrations or not.

The spectrum displayed in fig.6 was obtained for z = 0.03 mm. The most striking changes of the relative peak heights in the spectrum when z is increased, are (i) an increasing contribution of resonance emission from the excited level $\overline{6a^1}$ and (ii) a decreasing contribution of the emission from the relaxed combination level $\overline{16a^1\ 16b^1}$, leading finally to the disappearance of band no. 2 in the spectrum for z > 0.8 mm. On the other hand, the relative contributions of the emission bands 3 (originating from the molecular dissociation fragment) and 4 (originating from level $\overline{16a^2}$) to the total fluorescence intensity (which decreases because of the lower partical density further downstream of the nozzle) do not change significantly when z is increased. When the excitation is achieved in the blue wing of the $\overline{6a^1_0}$ absorption band (ν_{exc} > 18 812 cm^{-1}) the changes in the relative intensities of the emission bands exhibit a simular dependence on z, but these changes are considerably smaller. In the latter case the complex is prepared in higher vibrational states of the van der Waals modes than in the former case.

These observations indicate that the efficiency of the vibrational energy flow in the complex is slightly enhanced by collisions when the density of background levels is high, whereas the energy flow is completely collision-induced when the level density is low (cf. fig.4) as demonstrated by the example $\overline{6a^1} \rightarrow \overline{16a^1\ 16b^1}$. Intermolecular energy transfer during a collision compensates for the energy separation between initially prepared and final levels.

The z-dependence of the relative intensities can be understood qualitatively as being a consequence of decreasing collision frequencies and decreasing collision energies when z is increased. More experimental data are required to get quantitative information about collisional effects.

The relative intensities of the emission bands depend on both z and ν_{exc}. The data given in table 4 demonstrate the influence of the excitation frequency (bandwidth 0.1 cm^{-1}) on the efficiency of vibrational energy flow within the complex. For increasing values of ν_{exc} the intensity of resonance emission from the excited level $\overline{6a^1}$ decreases whereas the intensity originating from relaxed levels of the complex increases.

These observations are in agreement with the arguments given above, since an increase of ν_{exc} gives rise to the preparation of complexes in higher levels of the van der Waals vibrations (due to the excitation of higher members of the van der Waals sequence bands), which implies that the density of the van der Waals manifold in the final vibronic state is higher. As a consequence, the intramolecular energy flow to the final state is more efficient whether this process is collision-induced or not.

From the data given in table 4 it follows that the dissociation process yielding tetrazine in the $16a^1$ state becomes less efficient for increasing ν_{exc}. This is in agreement with the momentum gap law [8], as well as the energy gap law [2], which predict that vibrational predissociation (VP) is less efficient when the fragments are produced with more translational energy. A plausible explanation for the increasing yield of $T(16b^1)$ seems to be the increasing efficiency of the relaxation process $\overline{6a^1} \rightarrow \overline{16a^1 16b^1}$ which will be followed by a VP process $\overline{16a^1 16b^1} \rightarrow 16b^1 + Ar$ in which again one quantum of the 16a mode is transferred to the van der Waals bond, or by a VP process $\overline{16a^1 16b^1} \rightarrow 16a^1 + Ar$. Table 4 shows that the dissociation channel yielding $T(16b^1)$ is closed for the lowest value of ν_{exc} although energy is transferred towards $\overline{16a^1 16b^1}$. This indicates that only the dissociation process $\overline{16a^1 16b^1} \rightarrow 16a^1 + Ar$ takes place when the $\overline{16a^1 16b^1}$ level is prepared with hardly any excess energy in the van der Waals modes. Apparently, the energy of the 16b quantum is sufficient to break the van der Waals bond. If this dissociation process is not assisted by excess energy of the van der Waals modes in the $\overline{16a^1 16b^1}$ state, the energy of the 16b quantum is to be considered as an upper limit to D_0', i.e. 403 cm^{-1} for the $\overline{16a^1 16b^1}$ state. Energy transfer from the 16a mode to the complex bond can give rise to rupture of this bond only when the van der Waals modes have absorbed sufficient energy.

We have continued the time-resolved experiments [4] which have been

reported recently, using an improved method which allows the determination of rise and decay times of fluorescence signals on a subnanosecond timescale with higher accuracy than before. Details of this work will be published elsewhere[9]. The lifetimes of the S_1-vibronic levels of tetrazine are determined primarily by photodissociation of the molecule which gives rise to the formation of HCN and N_2. The quantum yield of the molecular photodissociation process is approximately unity [10]. The photodissociation rate appears not to be influenced by the formation of complexes T.Ar since the lifetimes of most of the vibronic levels of T and T.Ar are identical. Therefore it seems reasonable to consider the observed difference between the lifetimes of $T(16a^2)$ and $T.Ar(\overline{16a^2})$ as due to an additional decay channel (i.e. dissociation of the complex into T and Ar) which competes with the photodecomposition of the molecule. The rate constant for vibrational predissociation, k_{VP}, follows from the difference between the decay times. Very recently we have observed that the decay time of the $\overline{16a^2}$ level depends on the amount of excess energy ε_W stored in the van der Waals vibrational manifold. The magnitude of ε_W can only be estimated. A quantitative interpretation of the relation between ε_W and ν_{exc} is not yet possible since the structure of the excitation bands is not yet analysed in sufficient detail. Furthermore, ε_W might be reduced by collision-induced deactivation of the van der Waals vibrations.

For $\varepsilon_W = 0$ (direct optical excitation of the $\overline{16a^2}$ level) we have found $k_{VP} = 0.54 \times 10^9 s^{-1}$ and for estimated values of $\varepsilon_W \approx 175$ cm^{-1} and $\varepsilon_W \approx 250$ cm^{-1} we obtained rate constants $k_{VP} = 2.3 \times 10^9 s^{-1}$ and $k_{VP} = 0.95 \times 10^9 s^{-1}$ respectively ($\overline{6a_0^1}$ excitation).

The dissociation channel $\overline{16a^2} \rightarrow 16a^1 + Ar$ is closed for $\varepsilon_W = 0$, since the energy of one quantum of the 16a mode is less than D_0'. Only the dissociation channel $\overline{16a^2} \rightarrow 0^0 + Ar$ is energetically open. The latter channel is less efficient than the former one, according to the momentum gap law (or the energy gap law). Dissociation of T.Ar into $T(16a^1)$ + Ar will be possible for $\nu_w = 175\ cm^{-1}$ since 175 + 255 = 430 cm^{-1} probably exceeds D_0. When ν_w is increased to approximately 250 cm^{-1} the dissociation rate is reduced, which is again in agreement with the momentum gap law.

At present, detailed studies are carried out which are dealing with the dependence of the relative yields of relaxation and dissociation products upon the position of ν_{exc} within the absorption bands $\overline{16a^2_0}$ and $\overline{6b^2_0}$ of T.Ar. These studies are performed in combination with time-resolved measurements of selectively detected emission bands. From these experiments it follows that it is again the 16a mode which is involved in the VP process following optical excitation of the $\overline{6b^2}$ level.

Similar studies concerned with the complex $T.Ar_2$ are in progress. The data obtained after excitation of the $\overline{\overline{6a^1}}$ level of $T.Ar_2$ show that vibrational relaxation of this complex is more efficient than for T.Ar under the same experimental conditions (p_0 and z) and with corresponding positions of ν_{exc} within the absorption bands. The experiments with $T.Ar_2$ demonstrate that also in this case the 16a mode is involved in the principal dissociation channel.

ACKNOWLEDGEMENT

These investigations were supported by the Netherlands Foundation for Chemical Research (SON) and were made possible by financial support from the Netherlands Organization for Pure Research (ZWO).

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Table 1. Frequencies and symmetry species of some of the normal modes of s-tetrazine in the $S_0(^1A_g)$ and $S_1(^1B_{3u})$ electronic states.

vibration		1	4	5	6a	6b	16a	16b	17b
species		a_g	b_{2g}	b_{2g}	a_g	b_{3g}	a_u	b_{3u}	b_{3u}
frequency (cm^{-1})	S_0	1009	801	994	736	640	336	254	904
	S_1	755	365	366	703	362	255	403	681

Table 2. Spectral shifts of fluorescence excitation bands of T.Ar. The minus sign indicates a shift to the red with respect to the corresponding band in the excitation spectrum of uncomplexed tetrazine.

excitation band	$\overline{0^0_0}$	$\overline{16b^1_1}$	$\overline{16a^2_0}$	$\overline{6a^1_0}$	$\overline{6b^2_0}$
observed frequency (ν_{vac}, cm^{-1})	18105	18261	18629	18809	18888
shift (cm^{-1})	-23	-17	-8	-22	-24
estimated accuracy (cm^{-1})	$\pm$ 1	$\pm$ 1.5	$\pm$ 1	$\pm$ 1	$\pm$ 1

Table 3. Change of spectral position ν_{em} of emission bands resulting from a change of the excitation frequency ν_{exc}. Frequencies (ν_{vac}) and shifts are given in cm^{-1}.

ν_{exc}	18808.8		18812.3		18816.4
$\Delta\nu_{exc}$		+3.5		+4.1	
	ν_{em}	$\Delta\nu_{em}$	ν_{em}	$\Delta\nu_{em}$	ν_{em}
$\overline{6a^1_2}$	17336.5	+3.6	17340.1	+3.9	17344.0
$\overline{6a^1_0 16a^0_2}$	18138.1	+2.6	18140.7	+3.2	18143.9
$\overline{16a^2_2}$	17961.0	+1.0	17962.0	+1.3	17963.3
$\overline{5^1_1}$	17787.2	+2.5	17789.7	+1.1	17790.8

Table 4. Relative intensities of fluorescence bands after $\overline{6a^1_0}$ excitation of T.Ar. Relative intensities are normalized to 100 for the sum of the intensities. Excitation frequency (ν_{vac}) in cm^{-1}. Excitation bandwidth 0.1 cm^{-1}, z = 0.03 mm, p_o = 1.2 bar.

ν_{exc}	$\overline{6a^1_2}$	$\overline{17b^1_1}$	$\overline{5^1_1}$	$\overline{16a^1_1 16b^1_1}$	$\overline{16a^2_2}$	$16b^1_1$	$16a^1_1$
18808.8	38.8	(1)	3.9	5.0	14.3	0	38.4
18812.3	29.5	5.0	4.7	9.7	17.4	8.0	25.7
18816.4	14.6	5.2	6.3	13.8	23.6	14.4	22.1

CAPTIONS TO FIGURES

1. Schematic diagram of the T.Ar intermolecular potential for two different vibronic states of s-tetrazine. The levels of the van der Waals stretching mode are shown as well. Vibrational predissociation and vibrational relaxation of T.Ar are indicated by arrows a and b respectively.

2. Schematic representation of some normal modes of s-tetrazine.

3. Part of the fluorescence excitation spectrum of T.Ar near the $\overline{0^0_0}$ transition. Laser linewidth 1 cm^{-1}. Fluorescence was detected at 17369 cm^{-1} ($\overline{6a^0_1}$ transition), bandwidth 10 cm^{-1}, p_0 = 1.5 bar, z = 0.03 mm. The amplification factor has been changed from 1 to 20 beyond 10 cm^{-1} from the origin.

4. Schematic diagram of the T-Ar intermolecular potential for six vibronic states of s-tetrazine. The level schemes of the van der Waals stretching mode (ν_0 = 43 cm^{-1}) are shown. D_0' is assumed to be approximately 300 cm^{-1}.

5. Part of the fluorescence spectrum after excitation into the $\overline{6a^1_0}$ absorption band of T.Ar. The emission between 577 and 578 nm originates from the rotationally excited $16a^1$ level of the tetrazine fragment. The strong bands at 576.6 nm and 580.3 nm are due to the transitions $\overline{6a^1_2}$ (resonance emission) and $\overline{16a^2_2 6a^0_1}$ (relaxed emission) respectively. Detection bandwidth 10 cm^{-1}, p_0 = 1.3 bar, z = 0.05 mm.

6. Part of the fluorescence spectrum obtained after excitation of the $\overline{6a^1}$ level of T.Ar, ν_{exc} = 18808.8 cm^{-1}, laser bandwidth 0.2 cm^{-1}, detection bandwidth 15 cm^{-1}, p_o = 1.25 bar, z = 0.03 mm.
   Assignments:
   0: resonance emission from the $\overline{6a^1}$ level of T.Ar,
   1: $\overline{16b^1_1}$, 2: $\overline{16a^1_1 16b^1_1}$, 3: $16a^1_1$ (tetrazine molecule), 4: $\overline{16a^2_2}$,
   5: $\overline{17b^1_1}$, 6: $\overline{1^1_1}$ or $6b^1_1$, 7: $\overline{5^1_1}$.

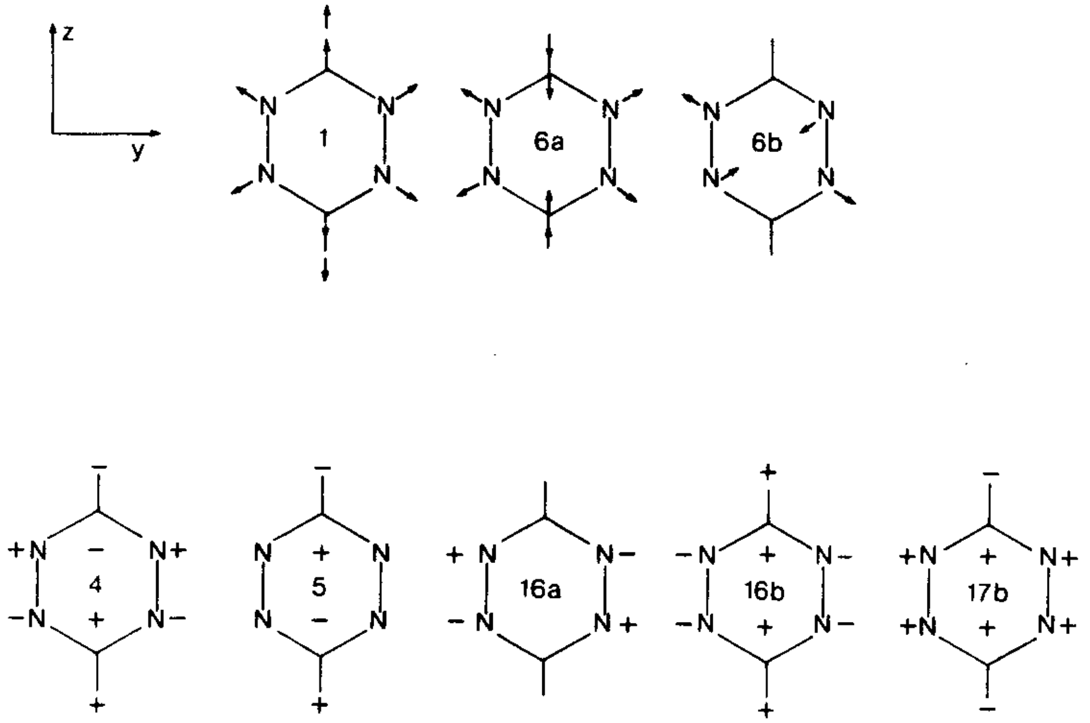


fig 2

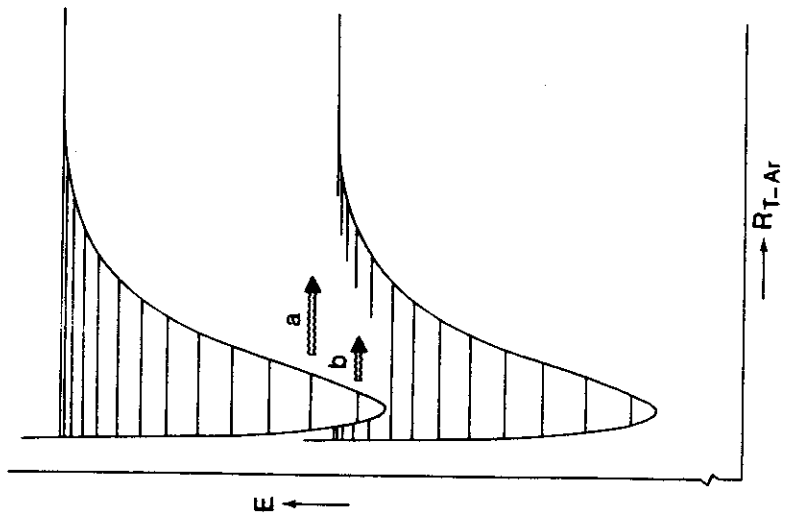
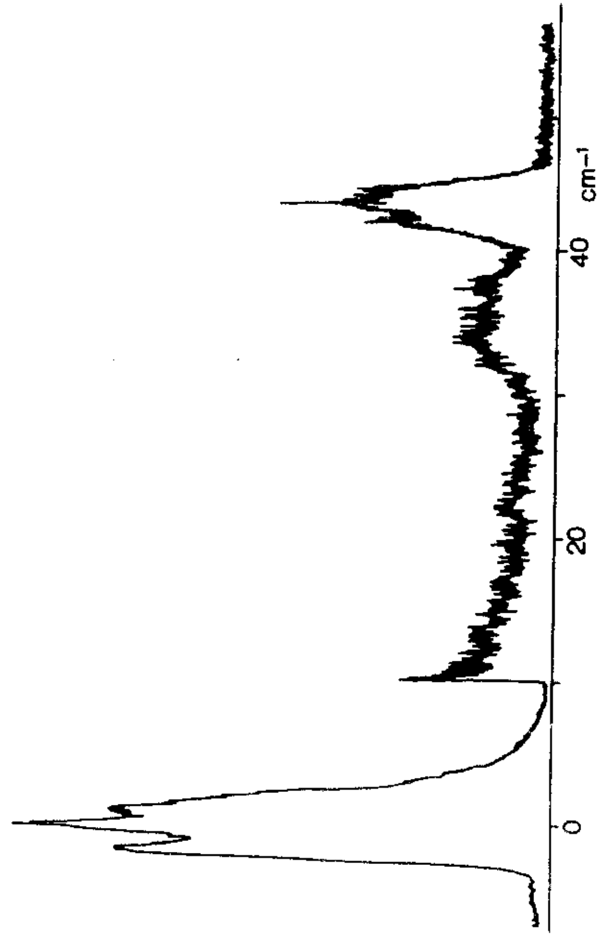


fig 1



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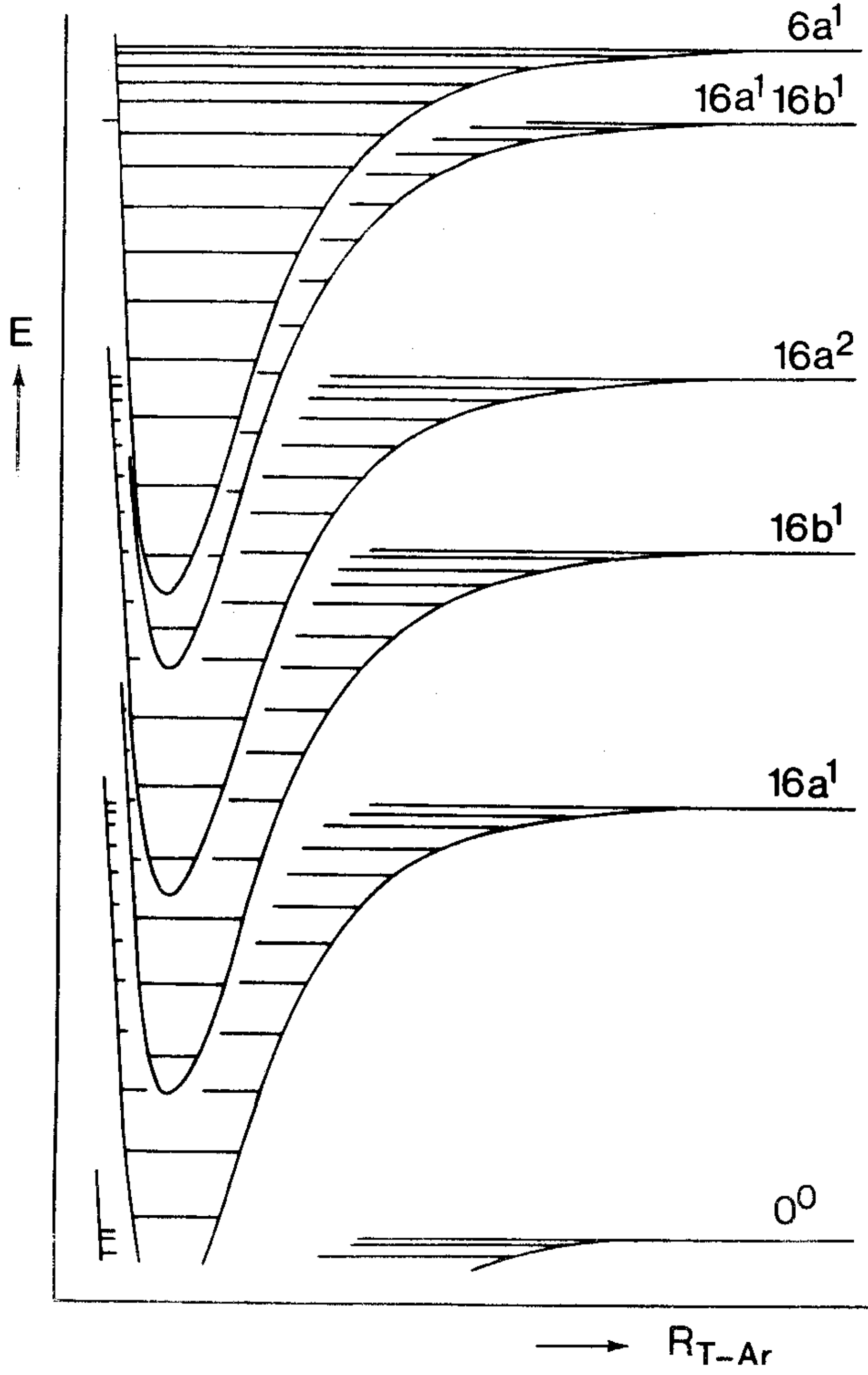

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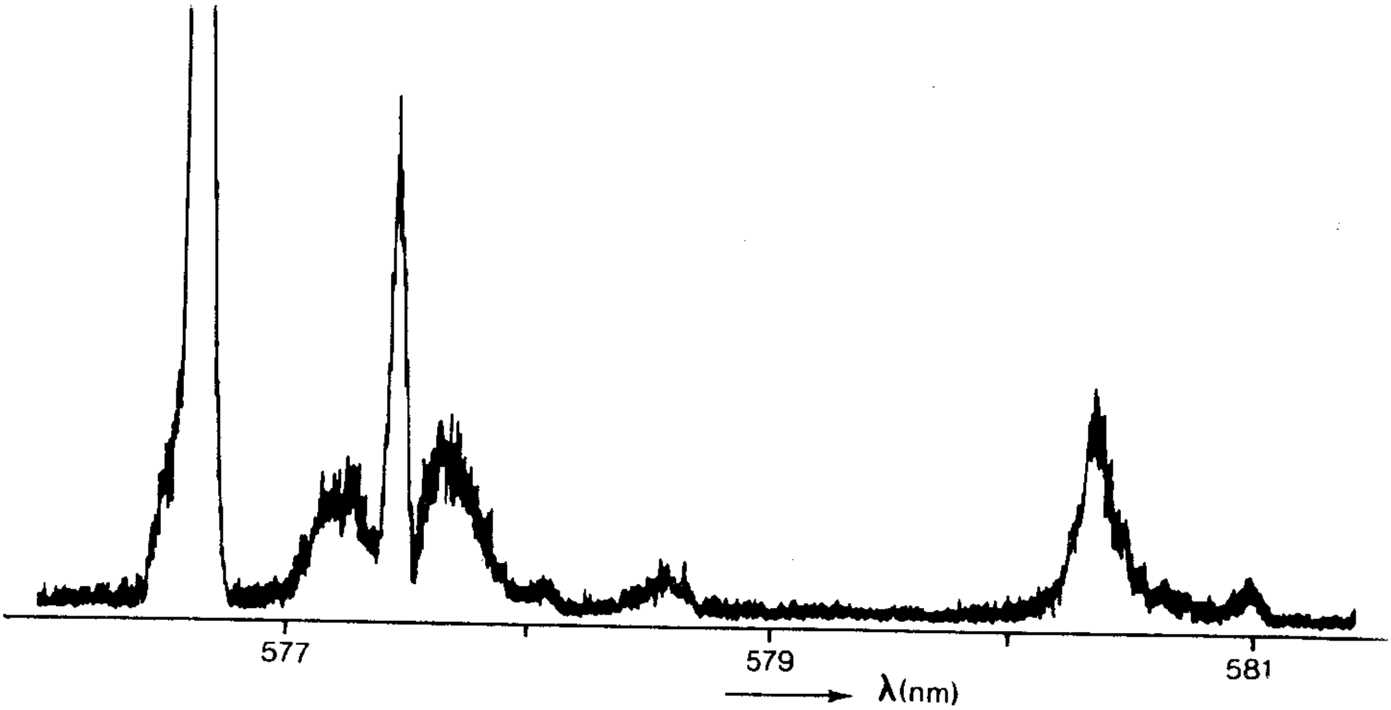

fig 5

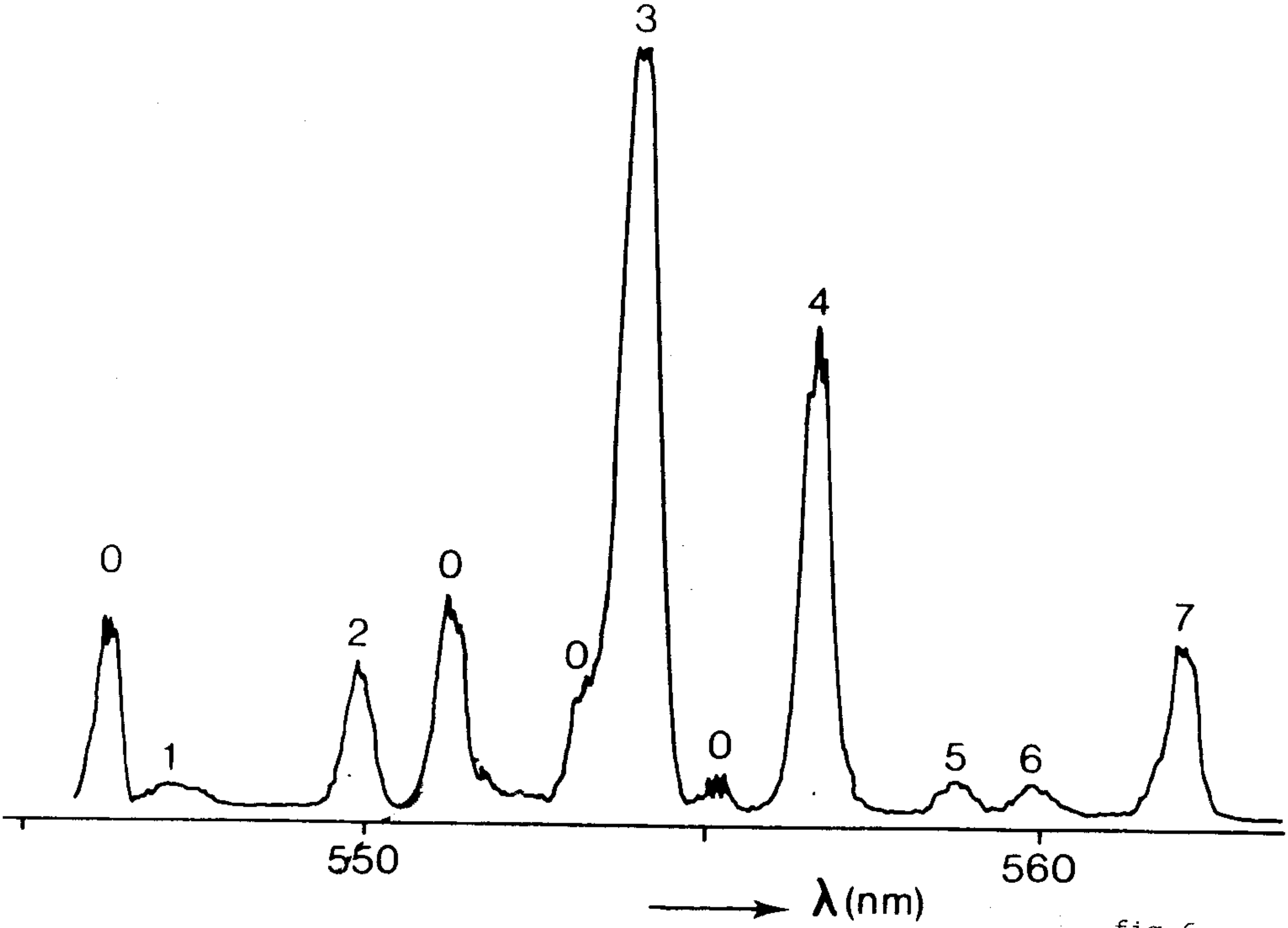

fig 6