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# Optothermal detection of non-radiative excited states of aromatic molecules in a molecular beam

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**Abstract**

Using a molecular beam laser spectrometer equipped with laser-induced fluorescence (LIF) and optothermal detectors, the high-resolution rovibronic spectra of large molecules, such as aniline, tetrazine and pyridine, were measured. The aim of this research was to demonstrate the ability of the optothermal detection technique to produce high-quality spectra, in particular in those cases in which the fluorescence quantum yield is so low as to render LIF detection practically impossible, e.g. pyridine. This technique reveals, in a direct manner, the energy transferred to vibrational and rotational degrees of freedom of the ground state after relaxation. In this sense, the optothermal spectrum is complementary to its LIF counterpart. The intensities of the spectral features in an optothermal spectrum are proportional to those in the absorption spectrum provided that the fluorescence quantum yield is small. © 1997 Elsevier Science S.A.

*Keywords:* Aromatic molecules; Molecular beam; Non-radiative excited states; Optothermal detection

## 1. Introduction

The effect of sequence congestion encountered in spectroscopic measurements of room-temperature gas phase samples can be eliminated if the experiments are performed in a seeded supersonic jet. Using this technique, the vibrational and rotational degrees of freedom of a large molecule can be cooled to very low effective temperatures with a corresponding reduction in the width of the Boltzmann distribution. Optical spectroscopy can benefit tremendously from this, by achieving a much higher resolution and great spectral simplification, especially when very high spectral purity, continuous wave (cw) laser sources, such as a ring dye laser or Ti:sapphire laser, are used. A further step towards higher resolution can be made by producing downstream of the supersonic expansion a well-collimated beam, which will allow sub-Doppler spectroscopy to be performed with an optical resolution of the order of a few megahertz in the visible or UV. The combined effects of a dramatic reduction of spectral congestion due to molecular cooling and a reduction in the inhomogeneous Doppler broadening permit relatively large molecules to be studied under very controlled (homogeneous) conditions, which can provide a wealth of new information to help unravel the fine details of the dynamics of the electronic excitations in these molecules. For example, using high-resolution sub-Doppler techniques, the work of Riedle et al. [1] (benzene) and van Herpen et al. [2] (pyrazine) clearly demonstrates the importance of molecular rotations in non-radiative decay processes, either intersystem crossing (ISC) or internal conversion (IC).

So far, with very few exceptions (mostly in IR spectroscopy) [3], all high-resolution molecular beam studies of intramolecular dynamics in isolated molecules, either in the time or frequency domain, have used molecular emission (fluorescence or phosphorescence) rather than (direct) absorption to follow the processes of interest. In the latter case, the basic limitation arises from the very low density of the molecules. In general, laser-induced fluorescence (LIF) is the method of choice for such studies, due to its extremely high sensitivity and intrinsic simplicity. However, generally speaking, if the molecules of interest are large, LIF becomes less and less attractive as the "dark" channels of energy relaxation start to compete more and more effectively with fluorescence.

With this in mind, the LENS molecular beam spectrometer has been designed with the capability of both LIF detection

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and optothermal (bolometric) detection [4] of the internal and kinetic energy content of the molecular beam.[2] The two detection techniques are almost complementary in that the energy lost by the molecule via fluorescence emission is no longer detected optothermally. It is then possible to follow, to a large extent, the fate of the energy initially deposited into the molecule (at present the detector is largely insensitive to phosphorescence photons emitted after ISC to the triplet state).

This paper reports a series of recent spectroscopic measurements performed on cold molecules in a beam, with the main aim of searching for the manifestation of non-radiative transitions. The molecules chosen cover a wide range of behaviour. Aniline, a system exhibiting a large fluorescence quantum yield and virtually no detectable spectral perturbations (which would be the sign of couplings between the initially excited $S_0$ state and the "dark" background states belonging to, for example, $T_1$ by ISC or $S_0$ by IC), is discussed first. *s*-Tetrazine and pyridine are also studied. Of the last two, the first exhibits efficient photodissociation after excitation to $S_1$, while still fluorescing with a small quantum yield ($\Phi = 0.001$) [5]. This is the first example of electronic excitation which can be studied by the optothermal detection technique with a sensitivity much higher than that possible with the LIF technique. Finally, pyridine is an example of a practically non-fluorescing molecule. The observation of its rotationally resolved spectrum was only possible due to the optothermal detection technique.

## 2. Experimental details

A detailed description of our experimental set-up has been given elsewhere [6]. Briefly, helium gas is normally used as carrier gas and mixed with the sample molecules. The resulting mixture is expanded through a nozzle of typically 100 μm diameter at a few atmospheres backing pressure. A molecular beam is extracted 12 mm downstream of the nozzle by a 0.4 mm diameter conical skimmer. Thus the rotational degrees of freedom are cooled to a temperature of a few kelvin.

The laser beam enters the vacuum chamber through two Brewster angle windows. Extensive baffling limits the amount of light scattered from the window surface which reaches the LIF detector. The total undispersed fluorescence is collected by two spherical mirrors and focused onto the active area of a photomultiplier tube. The signals are processed by photon counting.

Eventually, the molecular beam impinges on a liquid helium-cooled composite-type silicon bolometer target. The target is kept at 1.6 K by continuously pumping over liquid helium. At this temperature, its sensitivity is about $6 \times 10^5$ V $W^{-1}$. After several hours of operation, the time response of the bolometer deteriorates significantly due to the accumulation of frozen molecules on the surface. At a modulation frequency of 280 Hz and 0.1% molecular concentration in the cw beam, we obtain typically 8–10 h of useful measuring time. The bolometric signal contains a d.c. background due to the kinetic energy of the molecular beam. In order to remove the background and to extract the real signal, we used an amplitude-modulated laser field. The pre-amplified bolometric signal was processed by a digital phase-sensitive detector.

The molecules are excited with the fundamental (visible) or intracavity doubled (UV) emission of an actively stabilized ring dye laser (Coherent 699-21). The output power is of the order of 1 W in the visible range and 3 mW in the UV, approximately half of which is available at the crossing with the molecular beam. Automated single-mode scans can be made over a 1 $cm^{-1}$ interval in the visible range (2 $cm^{-1}$ in the UV). The laser linewidth is about 1 MHz in the visible (2 MHz in the UV). A typical spectrum covers several wavenumbers, and the full region is recorded by overlapping different single scans. A wavelength meter (Burleigh PWA) is used to ensure that the different sections overlap. A more precise absolute frequency calibration is obtained by recording the absorption spectrum of iodine in a static gas cell. Within a single scan, the relative frequency is calibrated against a 150 MHz etalon (temperature stabilized and hermetically sealed) [6]. The etalon FSR is accurately determined using ground state combination differences (if microwave data are available) or by the line separations in the iodine absorption spectrum.

## 3. Results and discussion

### 3.1. Aniline

We have recorded the molecular beam, fluorescence excitation and absorption (optothermal) spectra of the rovibronic bands of the $S_1(^1B_2) \leftarrow S_0(^1A_1)$ electronic transition in aniline at a resolution of 0.0005 $cm^{-1}$. In Fig. 1, the LIF spec-

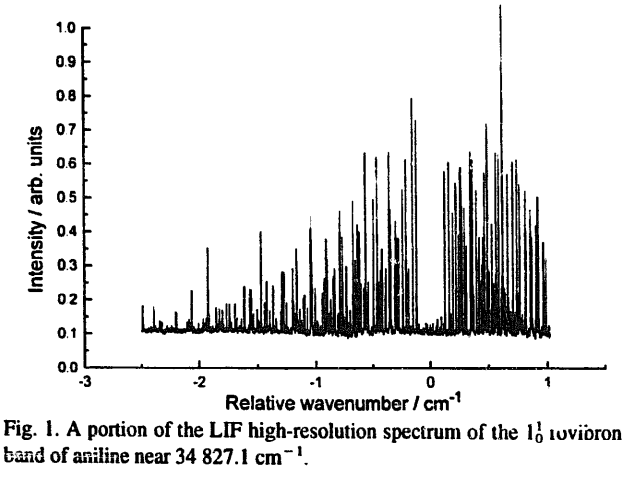

Fig. 1. A portion of the LIF high-resolution spectrum of the $1_0^1$ rovibronic band of aniline near 34 827.1 $cm^{-1}$.

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[2] The spectrometer was built in cooperation with Prof. G. Scoles (Princeton University, USA), Prof. D. Bassi and Dr. M. Scotoni (University of Trento, Italy).

trum of the $1_0^1$ rovibronic transition of aniline is shown. The $0_0^0$ transition, which occurs at 294 nm, is strongly allowed and polarized along the *b* axis in the plane of the ring and perpendicular to the C–N bond (*a* axis). The other three bands studied, $6a_0^1$, $I_0^2$ and $1_0^1$, occur at frequencies higher than the $0_0^0$ transition by 492.44 cm$^{-1}$, +760.80 cm$^{-1}$ and 797.89 cm$^{-1}$ respectively. The totally symmetric vibrations appear dominantly in both the absorption and excitation spectra. Only the $I_0^2$ band (*I* labels the inversion mode of the $NH_2$ group) involves a non-totally symmetric vibration of symmetry species $b_1$; the other species are all $a_1$. The observed transitions are fitted by a rigid asymmetric rotor hamiltonian model and no signs of perturbations are evident in the spectra. The individual lines appear equally homogeneously broadened, all requiring a lorentzian component of about 20 MHz to describe the experimentally observed profile.

Accurate rotational constants for the excited states of the rovibronic bands of the $S_1 \leftarrow S_0$ transition were determined [6,7]. Some assignments were confirmed by microwave–UV double resonance, an extremely useful tool for the analysis of complex spectra [8].

The absence of any perturbation in the spectra, even at a resolution better than 0.001 cm$^{-1}$, seems surprising. In pyrazine, with an $S_1$–$T_1$ energy gap of 4056 cm$^{-1}$, a density of states of about 150 per cm$^{-1}$ was sufficient to establish a strong perturbation [2]. In our case, the energy gap is larger (approximately 7200 cm$^{-1}$), and so the density of states at the vibrationless $S_1$ level is much higher (approximately $4 \times 10^5$ per cm$^{-1}$). However, the regularity of the asymmetric rotor spectra makes aniline similar, from the point of view of the photophysics, to large molecules such as benzene and naphthalene which also show high-resolution spectra of several vibronic bands well fitted to an asymmetric rotor hamiltonian.

Spin–orbit coupling between $S_1$($^1B_2$) and the lowest triplet state ($^3A_1$) is first order allowed, but rather weak due to the large energy gap (approximately 7200 cm$^{-1}$). Direct coupling to highly vibrationally excited states of $S_0$ is also usually very weak.

Such arguments agree with a high rate of fluorescence and low radiationless decay rate, and hence a relatively large quantum yield, as observed for aniline (0.28 or greater). The reported lifetime for the vibrationless $S_1$ state is 7.8 ns [9]. An irreversible decay on this timescale would lead to a 20 MHz lorentzian broadening of the rovibronic transitions. The analysis of the Voigt profile of our lines gives a homogeneous contribution of approximately 18 MHz.

Therefore we can conclude that, at least up to a vibronic energy of approximately 800 cm$^{-1}$ above the zero-point level of the $S_1$ state, aniline behaves as a large molecule in the statistical case of radiationless transitions, similar to naphthalene [10]. The good signal-to-noise (S/N) ratio exhibited by the optothermal spectra indicates that the most probable fate of the $S_1$ excited molecule is IC to highly excited vibrational levels of the electronic ground state.

### 3.2. *s-Tetrazine (ST) and dimethyl-s-tetrazine (DMST)*

There is continuing interest in the photochemical properties of the $S_1$ excited state of ST. It has already been demonstrated that, after excitation to the lowest energy excited state $^1B_{3u} \leftarrow {}^1A_g$ at 18 128 cm$^{-1}$, the molecule undergoes a concerted triple dissociation process leading to $N_2$ and 2HCN [11]. The properties of ST are well known. The photodissociation has an efficiency close to unity, while the fluorescence quantum yield is about 0.001 [5]. The spectroscopy of ST has been performed in bulb at room temperature, in a cold molecular beam and in low-temperature matrix isolation and neat crystal experiments. Nevertheless, uncertainty still exists about the homogeneous lifetime of the excited state, and the precise values of the rotational constants in both the ground and excited electronic states.

Substituted tetrazine shows a different behaviour depending on the nature of the substituents [12]. Usually a lower lifetime and a higher fluorescence quantum yield are reported. This suggests a drop in efficiency of the non-radiative processes.

Here, we focus our attention on ST and DMST. We measured the LIF and optothermal spectra of both molecules with the same molecular beam machine [13]. Sections of the ST $0_0^0$ transition are shown in Fig. 2.

The optothermal detector measures the amount of energy transferred from the molecule to the bolometer target. In this case, we obtain a signal either from molecules hitting the detector and releasing kinetic and adsorption energy in addition to the energy absorbed from the laser beam (positive signal) or, in the case of photodissociation, from the attenuation of the flow of molecules which reach the detector (negative signal).

A phase-sensitive detector will give both the amplitude and phase of the signal, revealing not only that the absorption of a photon takes place, but also the nature of the relaxation process, to the extent that we can easily distinguish between IVR (in which case at least part of the energy remains in the molecular beam) and photodissociation. We established the

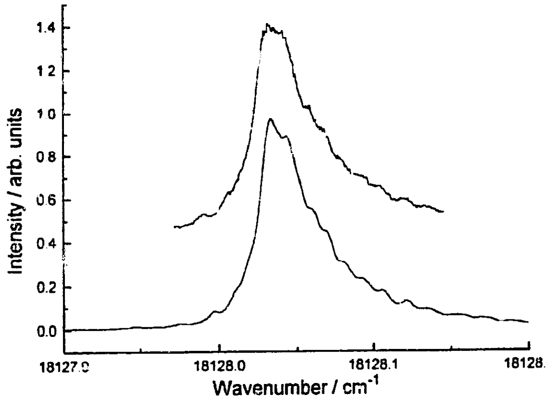

Fig. 2. Direct comparison of the LIF (upper trace) and optothermal (lower trace) spectra of *s*-tetrazine for a small portion of the $S_1 \leftarrow S_0$ $0_0^0$ transition around the Q branch. The integration time used was ten times longer in the case of LIF detection.

dissociative nature of the relaxation processes in ST and DMST by comparing the sign of the optothermal signal with that induced by stray laser light: scattered laser light yields a signal of the same sign as that induced by stable molecules. In this way, we obtained, for the first time, direct evidence for the photodissociation of $S_1$ excited DMST.

The linewidth of the $S_1 \leftarrow S_0$ transition in ST is 215 ± 10 MHz, which was obtained by taking into account the effect of power broadening. The result is in good agreement with the value of 190 ± 10 MHz extracted by Kiermeier et al. [14] from their Doppler-free, gas phase experiment (for $J''=8$–15). Both the linewidth and fluorescence quantum yield are not dependent on the rotational quantum number.

The spectroscopy of DMST is more complex, with respect to ST, due to the presence of two methyl rotors (in para positions); we were unable to make assignments of transitions other than those involving the $m=0$ torsionless states. The linewidth is 34 MHz, corresponding to a lifetime of 5 ns, in good agreement with existing data [15].

### 3.3. Pyridine

Due to its extremely low fluorescence quantum yield of approximately $6\times10^{-5}$ [16], attempts to observe the pyridine $S_1 \leftarrow S_0$ transition have so far been limited to LIF studies at resolutions which exclude the possibility to resolve fully the rotational structure [17]. We therefore chose pyridine as an ideal candidate to demonstrate the power of the optothermal spectrometer.

The oscillator strength of pyridine is similar to that of ST [18], but there are two issues which make pyridine a far more challenging problem. The first is the different absorption region (UV for pyridine, visible for ST) and the correspondingly different laser powers available (differ by more than two orders of magnitude). The second is the different fluorescence quantum yield (a factor of 20 smaller for pyridine) which effectively excludes LIF as a detection method for pyridine.

However, the optothermal technique is well suited to the application of laser power enhancement techniques, such as multipassing the laser radiation between plane-parallel mirrors.

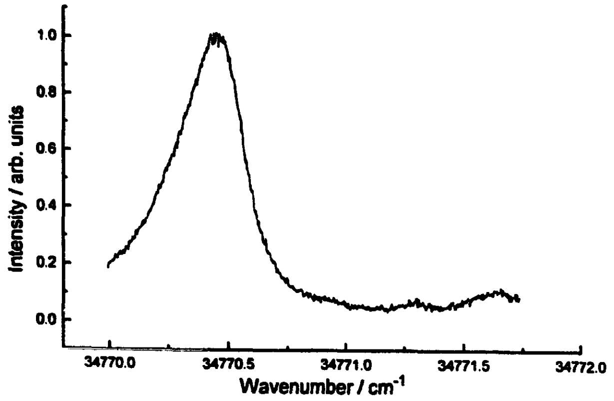

Fig. 3. The optothermal spectrum of the $S_1 \leftarrow S_0$ $0^0_0$ rovibronic band of pyridine near the Q branch.

Table 1
Some photophysical parameters derived for the investigated molecules

| Molecule | $\Phi$ [b] | $\Gamma$ (MHz) [a] | $\tau$ (ps) [a] | $\tau$ (ps) [b] |
|---|---|---|---|---|
| Aniline | 0.28 | 18 | 8000 | 7800 [8] |
| *s*-Tetrazine | 0.001 | 215 | 740 | 841 [11] |
| Dimethyl-*s*-tetrazine | 0.011 | 34 | 6000 | 6000 [20] |
| Pyridine | 0.00006 | 2200 | 70 | 30–60 [17] |

[a] This work.
[b] Existing data.

We recently succeeded in observing the $S_1 \leftarrow S_0$ 0–0 transition with rotational resolution at 288 nm using the optothermal method (Fig. 3) [19]. A preliminary analysis of the data reveals a largely homogeneous linewidth of approximately 2.2 GHz, corresponding to a lifetime of 70 ps. The latter is in fair agreement with the 30–60 ps excited state lifetime obtained in static gas cell time-domain experiments [20].

## 4. Conclusions

The importance of the optothermal detection technique, combined with cold molecular beam preparation and high spectral purity laser excitation, in the study of the photophysics of molecules exhibiting very efficient non-radiative relaxation channels has been clearly demonstrated.

Results are reported on the high-resolution spectroscopic observations of the first excited singlet electronic states of three molecules (aniline, tetrazine and pyridine), which differ strongly in their radiative to non-radiative quantum yield ratios, with the aim of demonstrating the ability of the optothermal technique to allow the measurement of high-resolution rovibronic spectra in the absence of fluorescence emission.

For aniline ($\Phi=0.28$), the two techniques, i.e. LIF and optothermal detection, have comparable sensitivities. For ST ($\Phi=0.001$), the LIF spectrum is still measurable, albeit with a much smaller S/N ratio with respect to the optothermal spectrum. Due to the nature of the optothermal detection method, the dissociative nature of the $S_1$ state has been clearly demonstrated for both ST and DMST. Finally, we succeeded in recording a high-resolution spectrum of pyridine for which previous attempts, using LIF detection, have failed.

Some photophysical data obtained for the three systems studied are collected in Table 1 together with relevant existing data.

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