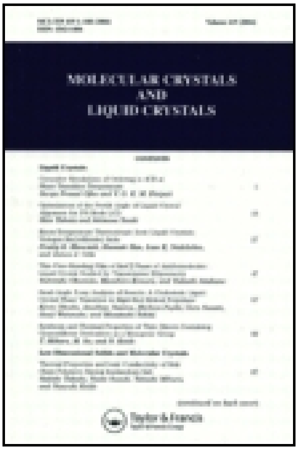

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Single Molecule Spectra of an Impurity Found in N-Hexadecane and Polyethylene

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SINGLE MOLECULE SPECTRA OF AN IMPURITY FOUND IN N-HEXADECANE AND POLYETHYLENE

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Abstract Impurities found in polyethylene and n-hexadecane give rise to intense and narrow single molecule lines at liquid helium temperatures. The fluorescence spectra of several impurity molecules in both matrices are nearly identical, suggesting that a single well-defined compound is involved. This paper summarizes all the photo-physical properties that may help identify the chemical structure of these impurities.

1. INTRODUCTION

A general trend of modern physical and chemical sciences is to study and manipulate ever smaller objects, with the ultimate goal of manipulating single molecules, ions and electrons. A first set of methods for working at the molecular level derives from the scanning tunneling microscope. More recently, a different approach has developed, with the spectroscopic isolation of single molecules. The principle of single molecule spectroscopy (SMS) is to record excitation spectra of small and dilute samples, where narrow lines of individual molecules are well resolved spectrally from one another at sufficiently low temperatures. By tuning a narrow laser to one of these lines, it is possible to effectively isolate one molecule in a volume of a few hundreds of cubic microns [1]. In well chosen host-guest systems, the signal/noise ratio is high enough to perform many kinds of experiments, such as lineshape studies, effects of external perturbations, magnetic resonance experiments, probing of spectral diffusion, etc. [2,3]. Among the possible applications of single molecule spectroscopy, an obvious one concerns chemical analysis and the detection of trace molecules. The isolation of intense lines of single molecules on a low background from matrix and non-resonant impurities implies a high discrimination ratio, which has not been exploited yet for chemical analysis. The interest of sharp zero-phonon lines is well known for bulk solutions, for which it leads to a very sensitive method of spectrochemical analysis [4].

The present work started as a search for new systems in which to study single molecules. We included Rhodamine 640, a laser dye, in polyethylene (PE). Although the combination of a polar, ionic dye with a non-polar matrix is not favorable to a strong zero-phonon line, we did observe a few strong and narrow lines in the region around 600 nm. Since their spectral position coincided with the overlap region of absorption and emission spectra of Rh640, we at first attributed them to a small fraction of dye molecules occupying special sites in the PE matrix. Later experiments, however, showed that the lines also occured in undoped PE samples, with the same features and average concentration. We then had to conclude that the lines originated from an impurity of PE. Parallel measurements on n-hexadecane Shpols'kii matrices also showed single molecule lines in the same spectral region, though with a much lower concentration than in PE. Again, the lines were present in pure n-hexadecane (HD) from the bottle. After checking that they were not experimental artefacts (like lines from the fiber used for excitation), we concluded that these lines stem from impurity molecules, called X throughout this paper, present at low concentration in PE and HD.

Despite detailed studies of the spectral features of these molecules, their chemical nature is still unknown. The main aim of this short report is to summarize all our data about molecule X, in order to facilitate its identification by the chemical community at large. Especially important are the wavelength of the 0-0 absorption in the non-polar solvents PE and HD, and the fluorescence spectrum with its characteristic frequencies and intensities, a true fingerprint of the molecule. Identifying molecule X would be very interesting for two reasons.

First, molecule X is particularly well suited to single molecule spectroscopy. We should stress here that SMS requirements are difficult to meet and that only a couple of molecular systems could be studied by this technique so far. The main ones are pentacene in p-terphenyl crystals [1], perylene [5] and terrylene in several matrices [6-9]. The conditions on the system for SMS studies are : a high fluorescence yield with a weak population of bottleneck states (such as triplet states in aromatics), the concentration of optical transition strength in a narrow zero-phonon line at liquid helium temperatures, a high photostability and a spectral range convenient for easy-to-use cw lasers. According to the results presented here, the unknown molecule X meets all SMS requirements perfectly. It could belong to a new class of molecules, quite different from the aromatic hydrocarbons used so far.

Second, X is present in two hydrocarbon matrices, both derived from natural oil, but processed in completely different ways. This suggests that it should be rather common. Since it can be detected with high selectivity and sensitivity, X could be used as a tracer, for example in environmental or forensic studies. This work is the first application of single molecule spectroscopy to the detection and, we hope, the eventual identification of natural trace impurities.

2. EXPERIMENT

Most of the measurements reported here were made with our original setup for the spectroscopy of single molecules, described in [10]. The sample is fixed at the end of a single-mode optical fiber and the fluorescence is collected with a parabolic mirror. The advantage of this design is that adjustments are minimal, which is important for a quick scanning of new samples. We recorded the fluorescence spectra of X molecules using the confocal excitation design described earlier [11], and dispersing the emitted light in a spectrograph. Although the adjustments are more difficult than with the fiber, the much improved optical quality of the fluorescence beam is critical for efficient transmission through a spectrometer slit. One of the difficulties of working with very low concentrations of molecules is that molecules in the focal spot of the mirror are very rare. Therefore, one must work with out-of-focus molecules, whose coupling to the spectrograph slit is poor. The signal-to-noise ratio of such emission spectra is therefore poorer than those of single pentacene molecules [11], although the emission rate of X is much higher.

Once we realized that X molecules were impurities of the solvents, we used them without doping. Polyethylene was purchased from Aldrich (high density, crystallinity 75%, MW 125000). The first sample of hexadecane was from an old bottle from Aldrich. Among the hexadecane samples, this one had the highest concentration of X. Other qualities of hexadecane were tried (Fluka, and a fresh bottle from Aldrich), where X molecules were also found, but with much lower concentration.

3. RESULTS

We attempted to extract the X molecules from PE, where their concentration is relatively high, using spectrograde methylcyclohexane as a solvent in which the polymer swells. We recorded fluorescence and excitation spectra of the extract. When excited at 550 nm at room temperature, the extract emitted a broad band between 577 and 600 nm with a peak at 596 nm. Both the emission and the excitation bands being very broad, it was impossible to attribute them to X molecules only. Since the concentration was too low to separate the X molecules in a single operation, the traditional methods of analytical chemistry were difficult to apply. Therefore, the results presented here were obtained on single molecules only. We first discuss the spectra of single X molecules in the Shpol'skii matrix HD, then in the polymer PE.

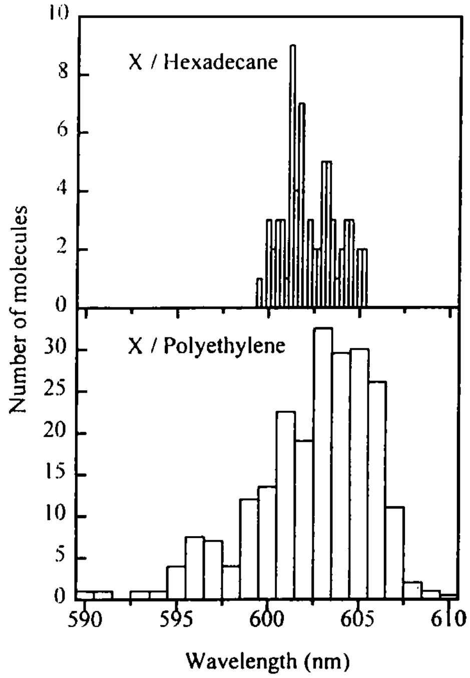

Figure 1: Histogrammes of resonance frequencies of single X-molecules in hexadecane (top) and polyethylene (bottom). The top spectrum shows an accumulation of lines around 602 nm, perhaps corresponding to a site of X in hexadecane. The poor statistics of the hexadecane histogramme are due to the very low concentration of X in this solvent. The histogramme is cut off abruptly because we did not investigate the outer range systematically. The lower histogramme shows a rather broad inhomogeneous band, characteristic of a polymer. The width of the band is similar to that for terrylene in PE, but the origin of its asymmetrical shape is an open question.

3.1 X-Impurity in Hexadecane

The first interesting parameter of X impurities is their absorption wavelength. Figure 1 shows a histogramme of the wavelengths of single molecule lines observed on systematically scanning the spectral interval from 600 to 605 nm. There were lines outside this interval as well, but since our exploration was not systematic, they are not included in Fig1. The histogramme is a small section of the excitation spectrum of X in HD, containing the contribution of the zero-phonon lines only. It shows a rather uniform distribution of lines, with an accumulation close to 602 nm, perhaps corresponding to a site of X in HD. The poor statistics are due to the low concentration of X. The number of lines can be used to give a very crude estimation of the order of magnitude of the concentration of X in HD. A precise estimation is impossible because HD scatters light strongly, and the illuminated volume is unknown. From upper and lower bounds for the volume, we conclude that the concentration of X in HD lies between 10^{-12} and 10^{-9} mole/l.

The next parameter we studied was the width of the single molecule lines. The corresponding histogramme is drawn in Fig2. Because these lines are fairly narrow in HD, we used the frequency stabilization described in ref.[10], to eliminate broadening by laser drifts, and decreased the power to avoid saturation broadening (see below). Because this procedure was lengthy, the histogramme includes only a few lines. No line was narrower than 35 MHz, which could be the lifetime-limited width of X, and the maximum measured width in HD was about 65 MHz. The upper bound of 35 MHz for the lifetime-limited width gives a lower limit of about 4 ns for the S_1 lifetime of X. Because the fluorescence yield must be high, such a short time indicates a strongly allowed transition. The two spectra of Fig2 are examples of single X lines, showing the high signal/noise ratio achievable at higher intensity, while power broadening is still insignificant. On the whole, the histogramme of widths, although peaked at lower widths, is not unlike that of terrylene in HD [12] (the lines of [12] were recorded without frequency stabilization).

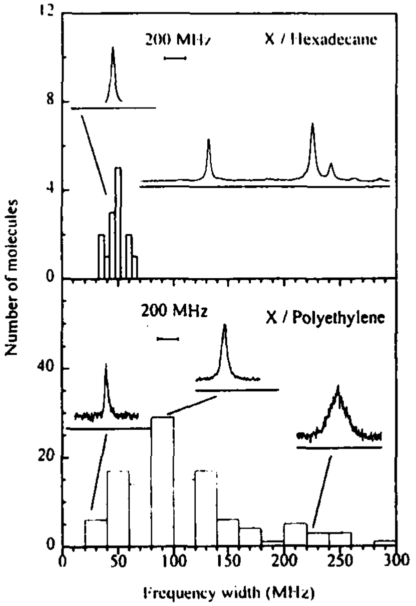

Figure 2: Histogrammes of widths of single X-molecules in hexadecane (top) and polyethylene (bottom). The distribution in the crystalline matrix is peaked around 50 MHz, with a lower limit of 35 MHz, perhaps corresponding to the natural linewidth of X. The distribution is considerably broader in the polymer matrix (as for terrylene in PE), but there is a sharp cutoff at about 40 MHz. Some typical lines are presented as insets with the histogrammes. The lines of X in hexadecane have been recorded at high intensity to decrease the noise, one of them on a 200 MHz scan width with a frequency stabilization of the laser. The several lines of the other spectrum might belong to only one molecule, since all of them had the same (very high) stability versus intensity and temperature increases up to 9 K.

Some of the X molecules in HD jumped in frequency, but most of them were very stable, enough to study their saturation behavior. Two lines were particularly resistant (they are shown as insets in Fig2), and did not jump even at an exciting power of 6 mW, corresponding to 40 W/cm^2 if the molecule was just at the fibre output. These lines only showed a slight broadening at this high power. Since the location of the molecule is not known, the saturation intensity cannot be calculated, but the study of the fluorescence signal as a function of the width leads us to a maximum *detected* count rate of 800000 per s at full saturation! This very high rate, comparable to that of terrylene [9,13] gives an upper bound of about 10 ns for the life-time of the excited state S_1 of X (assuming an upper bound of about 1% for our overall detection efficiency). This indicates that the triplet manifold is not an efficient bottleneck in the saturation of X, i.e. that the intersystem crossing is very weak and/or the triplet lifetime is very short.

We also checked the temperature dependence of the linewidth, which probably is more characteristic of the crystalline HD matrix than of the X molecule. We found no significant broadening effect below 5 K, and a steep broadening above 5 K, which could be well fitted by an exponential activation, as is often the case in molecular crystals [14].

We now turn to the fluorescence spectra of X in HD. Because of their complex structure with many lines, these spectra are the most stringent features to characterize X molecules. These spectra were recorded with a slit width of 100 mm, corresponding to a resolution of about 7 cm^{-1}. The upper spectrum of Fig3 presents the fluorescence spectrum of a single X-impurity in HD. The emission spectra of the 7 different X molecules we recorded were remarkably similar, apart from splittings of a few modes for one of them. This points to a rather homogeneous population of impurity molecules, rather than to a mixture of isomers or of differently substituted compounds. An important part of the fluorescence is emitted around 1400 cm^{-1} below the excitation, which would be expected if X was an aromatic molecule. A fairly large intensity is contained in the several low-frequency modes between 300 and 700 cm^{-1}. A list of the frequencies of the strongest modes with their intensities is given in Table 1. This spectrum is different from those of pentacene and terrylene [11,15], which excludes an accidental contamination by one of these molecules in our laboratory, and is also different from those of many common polycyclic aromatic hydrocarbons in Shpol'skii matrices [16] (not surprisingly, since most of them have their absorption maximum at waves shorter than 500 nm). Comparing the emission spectrum of the impurities of PE (lower spectrum of Fig3) with that of X in hexadecane, we are struck by their general resemblance, by the coincidence of the frequencies of most lines and of their intensity ratios. Some slight differences between these spectra will be discussed below, but we conclude from their similarity that they both arise either from the same molecule, or from very close molecules, perhaps differing by substitutions. In the rest of this paper, we therefore discuss the impurities of PE assuming that they are the same X molecules as in HD.

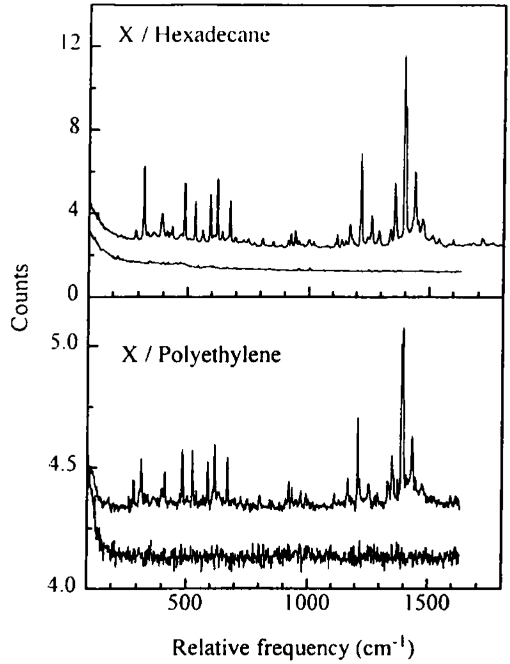

Figure 3: Fluorescence spectra of single X-molecules in hexadecane (top) and polyethylene (bottom). The spectra are compared to background spectra, recorded with the excitation out of resonance with the excitation line. The complete absence of even strong molecular lines on these spectra proves that the fluorescence indeed arises from single molecules. The signal/noise ratio was less in the polymer case because photo-induced jumps limited the acquisition time. The similarity of both spectra strongly supports the attribution of both to the same molecule, or to slight variants thereof. This "fingerprint" spectrum could be used to identify X by comparing it to known fluorescence spectra of bulk solutions.

3.2 X-Impurity in Polyethylene

The histogramme of the frequencies of single molecule lines in PE is shown in Fig1 (lower part). By the same argument as above, we estimated the concentration to between 10^{-10} and a few 10^{-9} mole/l. Because of the higher concentration, the statistics are better than for HD. As expected for a strongly disordered environment, the corresponding inhomogeneous band is broad and structureless, similar to the inhomogeneous band of terrylene in PE. A striking feature of the distribution is its asymmetry, with a broad wing on the blue side. We have no explanation yet for this asymmetry. The range of wavelengths of these excitation lines is compatible with that in HD, assuming that the same impurity is included in both matrices.

TABLE 1: Vibrational frequencies (in cm^{-1}) and intensities (normalized to that of the vibrational line at about 1214 cm^{-1}) of some fluorescence lines of single X molecules in hexadecane and polyethylene at 1.8 K. The low-frequency intensities have not been corrected for the transmission of the notch filter. The frequency resolution is about 7 cm^{-1}. The intensities, measured at the maxima of the lines, are subject to a fairly high inaccuracy for the PE data (see Fig3).

X/HD		X/PE	
Frequency	Intensity	Frequency	Intensity
290	0.10	288	0.30
322	0.79	318	0.55
395	0.25	-	-
-	-	412	0.34
487	0.60	483	0.64
530	0.44	525	0.66
562	0.13	-	-
592	0.48	589	0.51
622	0.67	618	0.70
675	0.44	671	0.57
923	0.15	922	0.26
942	0.17		
1117	0.15	1111	0.15
1172	0.23	1168	0.30
1218	1	1210	1
1262	0.33	1255	0.21
1296	0.17	-	-
1356	0.63	1351	0.47
1394	1.7	1389	1.3
1401	0.9	1396	1.5
1438	0.67	1435	0.60
1469	0.19	-	-
1599	0.1	1593	0.13

We also measured the histogramme of linewidths for X in PE. The results are shown in Fig2 (lower part), with a few examples of single molecule lines with different widths. The cutoff of this distribution is around 40 MHz, i.e. it corresponds to the narrowest lines in HD. The distribution includes much broader lines, which is characteristic of dynamics in PE, and results in a picture very similar to that of terrylene in PE [17].

The photostability of the X molecules in PE was comparable to that of terrylene in PE. It was possible to resonantly excite the molecules during a few minutes on average with an intensity of about 30 mW/cm^2, but the long acquisition times and high intensities we applied to X in HD were forbidden here. This might be a feature of the disordered environment of PE, where repeated excitation of a molecule might induce jumps of nearby defects (two-level systems [17]).

The emission spectrum of X in PE shown in Fig3 is very close to that of X in HD, as discussed above. The signal/noise ratio is poorer, in spite of the higher concentration (the light collection should improve because we can select molecules closer to the focus). This is because the acquisition time and the exciting intensity were limited by photo-induced processes. Again, the spectra of several molecules in PE are very similar to one another, within experimental noise, a hint that a well-defined compound is concerned. There are a few systematic differences from the spectrum of X in HD. First, the intensities of the two components of the split central mode at 1400 cm^{-1} are different. Apart from weak lines which might disappear in noise, a few lines of X/HD are absent for X/PE (see Table 1), for example the lines at 395, 562, 1296 and 1469 cm^{-1}, and vice versa with the line of X/PE at 412 cm^{-1}. It is difficult to ascribe such small differences either to a chemical difference or to differences in the "sites" that X occupies in the two matrices, which might break one of its symmetries [18]. Nevertheless, the overall agreement between frequencies and intensities is as good as experimental errors allow, supporting the conclusion that the impurities in HD and PE are either identical or at least very closely related.

4. CONCLUSION

Finally, what conclusions can we draw from our observations concerning the nature of the X molecule? The molecule must absorb at 600 nm, and might therefore be a large aromatic hydrocarbon. This is supported by a strong 1400 cm^{-1} mode in the fluorescence spectrum. To our knowledge, none of the well known aromatics can match its emission spectrum. The red transition of the X molecule is strong (with a lifetime of 4 to 10 ns), its fluorescence yield is high, with no significant triplet bottleneck. Since we observed the X molecule in solvents purchased from different companies, we think that it must occur naturally as a trace impurity of many hydrocarbons. While hoping that the publication of these results will help identify X, we plan to extract a larger quantity of X from polyethylene in order to apply more classical analytical methods.

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