

Vibrational predissociation in weakly-bound clusters: A dispersed fluorescence study of toluene rare-gas complexes

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Abstract

The vibrational predissociation (VP) dynamics of toluene-Ar and toluene-Ne complexes have been investigated using single vibronic level fluorescence spectroscopy. For several levels, comparison of the dispersed fluorescence spectra with those from monomer levels permits the identification of the final monomer vibrational level. Pumping of the low-lying S_1 $\overline{13_0^1/24_0^1 25_0^1}$ or $\overline{37_0^1}$ transitions in toluene-Ar, for example, gives rise to efficient VP leaving the resulting toluene monomer in its vibrationless S_1 state. By contrast, in the case of toluene-Ne, VP following $\overline{37_0^1}$ level pumping leaves the toluene molecule in an excited $\overline{16^1}$ level which is optically inaccessible from the ground state.

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I. Introduction

Weakly-bound molecular clusters can provide ideal environments within which to study the fundamental process of vibrational energy relaxation which lies at the heart of chemical reactivity.[1] In some cases, the understanding of the vibrational structure in low-lying electronic states is sufficient to permit the excitation of individual well-characterised levels from which vibrational energy flow may be observed. In van der Waals systems, intramolecular vibrational redistribution (IVR) by which the initial excitation is transferred from the chromophore into the intermolecular modes, can be relatively slow. This reflects the considerable mismatch in frequencies between the chromophore intramolecular modes and the intermolecular modes.[1,2] Once significant vibrational energy reaches the van der Waals mode, vibrational predissociation (VP) often follows rapidly, resulting in the breaking of the intermolecular bond. In general, VP takes place on the same electronic surface and, in well-characterised systems, dispersed fluorescence studies have revealed a detailed picture of the overall process by permitting identification of the final fragment quantum states. We have applied this single vibrational level excitation / dispersed fluorescence approach to the rare gas clusters of toluene.

The convenience, in the near UV, of the $S_0 - S_1$ transitions in aromatic molecule-X complexes (X = rare-gas atom, small molecule), coupled with the large fluorescence quantum yield of the S_1 states, has long made these molecules particular favourites for IVR/VP studies. Dispersed, or single vibrational level, fluorescence spectroscopy has been applied to the study of VP in rare-gas clusters of benzene,[3] aniline,[4,5] *s*-tetrazine,[6,7] *p*-difluorobenzene (*p*-DFB),[8,9] *p*-fluorotoluene(*p*-FT)[8] and aminophenol[10]. For low-lying S_1 vibrational levels, the overall VP process has often been found to be mode-specific reflecting the considerable variation in IVR rate following excitation of different vibrational modes.

The toluene-X (X=Ne, Ar) van der Waals molecules allows us to study two features which have previously been shown to play a profound role in IVR/VP dynamics. Firstly, the low-frequency

methyl group torsional modes have been implicated as leading to the vastly enhanced IVR rates exhibited by some molecules upon methyl-substitution.[11-13] This is particularly dramatic in *p*-FT for which the FT final state distribution is essentially statistical with no sign of the highly mode-selective distribution observed, e.g., in *p*-DFB.[8] It is believed that, during the motion associated with the methyl group rotation, repulsion between the methyl group and atoms of the ring results in ring puckering which significantly enhances the IVR rate.[11,13,14] Secondly, the effects of different cluster partners can be explored. In aniline clusters with Ar, N₂ and CH₄ the rate of IVR has been shown to increase enormously with the number of degrees of freedom of the cluster partner (and hence the density of states) resulting in final state distributions which are increasingly statistical in character.[4,5,15] Even clustering with different rare gas atoms can have a dramatic effect on IVR rates. The Parmenter group have studied *p*-DFB –X (X=Ar, Ne, N₂) clusters in great detail[8,9,16] and have shown that, by contrast with the Ar- and N₂- complexes, the overall dissociation kinetics in Ne-*p*-DFB is often too slow to compete with fluorescence.

The *S*₁-*S*₀ transition in the isolated toluene molecule has itself received much spectroscopic attention.[17-23]. Of most direct relevance to the present study is the detailed fluorescence excitation and dispersed fluorescence of Hickman *et al.*[19] which characterised all strong features in the fluorescence excitation spectrum within 2000 cm⁻¹ of the origin band. Of relevance to what follows, Hickman *et al.* observed the onset of significant IVR, signified by the growth of a broad unresolved feature in the dispersed fluorescence spectra, to be in the region of the 12₀¹ / 23₀¹24₀¹ transition.

In a previous fluorescence excitation study of toluene-X complexes (X=Ne, Ar, Kr),[24] we investigated the effect of complexation with rare gas atoms on the lifetimes of low-lying *S*₁ levels. In particular, we examined the microscopic external heavy atom effect on the *S*₁ 0⁰ levels and proposed that the reduction in lifetime observed with increasing mass of the cluster partner arises from enhanced intersystem crossing, an interpretation since supported by multiconfigurational

linear response calculations of the spin-orbit coupling in these systems.[25] Experimentally, the fluorescence lifetimes of complex levels were observed to generally decrease with increasing mass of the rare-gas cluster partner. However, several anomalies were observed in which the apparent fluorescence lifetime observed following excitation of cluster levels was longer than that of the corresponding monomer level. It was these findings which prompted the present study.

II. Experimental Details

The experimental apparatus used for these studies is a slightly modified version of the conventional pulsed molecular beam / laser induced fluorescence experiment used for our earlier fluorescence excitation study of the same complexes and those of *p*-DFB.[24,26] In order to record the single vibronic level fluorescence (SVLF) spectra, fluorescence was collected mutually perpendicular to both the laser and molecular beams and focussed onto the entrance slits of a simple, medium resolution scanning monochromator (Oriel Instruments, Cornerstone 260, 1/4 m; max. resolution = 0.15 nm). Signals were detected after the exit slits by a photomultiplier tube (Electron Tubes, 9813QB) fitted with quartz window. Due to the low number densities of some of the cluster species the choice of monochromator slit widths was a necessary compromise between signal intensity and spectral resolution (*ca.* 40 cm⁻¹). To permit comparison and aid assignment, however, the same slit width was used in recording both cluster and monomer dispersed fluorescence spectra. Signals were processed by an oscilloscope (Lecroy Waverunner LT342) and transferred to a PC via an Ethernet link. Some effort was made to gate different temporal regions of the fluorescence decay in an attempt to record time resolved fluorescence but the signal to noise ratio achieved was insufficient to infer anything conclusive.

Toluene of 99% purity was supplied by BDH and utilised without any further purification. Rare gases were provided by BOC and were 99.999% pure with the exception of helium, which was 99.996% pure. Toluene was seeded in the rare gas carrier at sufficiently low concentration (~0.1%)

to minimise complications arising from the toluene dimer. The signals due to the van der Waals complexes of interest were optimised (with respect to composition and backing pressure) by detailed curve of growth studies while recording fluorescence excitation spectra. Again, to aid comparison the SVL fluorescence spectra of the complexes and the monomer were recorded under identical conditions.

III. Results and Discussion

The S_1 - S_0 fluorescence excitation spectrum of the toluene monomer in the region 0^0 to $0^0 + 2000$ cm^{-1} is shown in Figure 1. This spectrum was obtained by expanding toluene in helium, with which no obvious clustering takes place. The inset in Figure 1 shows a portion of the spectrum around the $13_0^1 / 24_0^1 25_0^1$ transition recorded in an argon expansion clearly showing additional peaks originating in toluene-Ar van der Waals complexes. The identity of these peaks was confirmed by detailed curve of growth and fractional composition studies[24]. The energy level diagram, Figure 2, shows the relative positions of both monomer and cluster S_1 vibrational levels salient to what follows. The relative stabilisation energies are taken from our own CASPT2 calculations.[25]

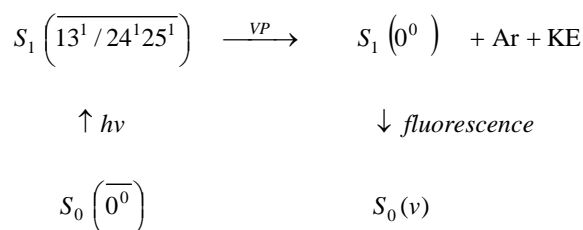
A. $\overline{0^0}$ level SVLF spectra

Figure 3 shows the dispersed fluorescence spectra of the toluene-Ne $\overline{0^0}$ and toluene-Ar $\overline{0^0}$ levels, where the horizontal bar indicates levels (or transitions) in the complex. For comparison, the SVLF spectrum of the toluene monomer 0^0 level, recorded under identical conditions is also shown. Unsurprisingly, the spectra of both complexes are essentially identical to the corresponding monomer spectrum except for the small red-shift (*ca.* 3 cm^{-1} for Ne and 25 cm^{-1} for Ar) resulting from complexation. At this resolution, it is tempting to interpret some of the minor peaks in the toluene-Ar spectrum as arising from progressions in the van der Waals stretch and certainly some of the line positions would support such an interpretation. However, conclusive assignment must await

a higher resolution study. No such additional peaks are visible in the toluene-Ne $\overline{0^0}$ spectrum. The assignments indicated in the lower graph are taken from the SVLF spectrum of the monomer by Hickman *et al.*[19] The fluorescence lifetimes of the vibrationless levels are given in Table 1 and illustrate the microscopic heavy atom effect by which the S_1 lifetime is significantly reduced by clustering with increasingly heavy partners as the intersystem crossing rate is enhanced.[25]

B. The Ar-Toluene $\overline{13^1/24^125^1}$ SVLF spectrum

The first vibrationally excited level from which it was possible to record cluster SVLF spectra was the $\overline{13^1/24^125^1}$ Fermi resonance and the spectrum of the toluene-Ar complex is given in Figure 4. Spectral congestion in this region, unfortunately precludes the observation of the neon complex in the fluorescence excitation spectrum. In the upper part of Figure 4 the spectrum of the complex is compared with that obtained from the corresponding monomer level and it is clear that the two spectra bear little similarity. By contrast, the spectrum from this particular complex level shows excellent agreement with that recorded from the monomer 0^0 level as shown in the lower part of Figure 4. The implication, then, is that the toluene-Ar $\overline{13^1/24^125^1}$ level is subject to rapid VP resulting in electronically excited toluene in its vibrationless ground state. That is,



This interpretation is consistent with apparent fluorescence lifetimes observed in the fluorescence excitation spectrum (see Table 1)[24]. The lifetime recorded following pumping of this cluster level (82.1 ± 0.8 ns) was found to be essentially the same as that for the monomer 0^0 level (85.7 ± 1.1 ns) and somewhat longer than that observed for the monomer $13^1/24^125^1$ level (69.2 ± 3.7 ns).

C. $\overline{37^1}$ SVLF spectra

Figure 5 shows the SVLF spectrum following pumping of the $\overline{37_0^1}$ transition in toluene-Ar. It is clear that VP leaves the toluene predominantly in its S_1 0^0 level. Once again, this explains the fluorescence lifetime observed following pumping of the toluene-Ar $\overline{37^1}$ level (82.6 ± 2.2 ns) matching that of the toluene monomer 0^0 level (85.7 ± 1.1 ns), rather than the 70.7 ± 1.9 ns of the toluene monomer S_1 37^1 level.

For this level it was possible to record a SVLF spectrum from the toluene-Ne $\overline{37^1}$ level and this is shown in Figure 6. Again the spectrum shows little similarity to the spectrum from the corresponding monomer level but this time the agreement with the spectrum of the monomer 0^0 level is also poor. Whilst there is some evidence of fluorescence around the position of the monomer 0_0^0 transition at 37477 cm^{-1} , the first strong peak in the spectrum (at *ca.* 37300 cm^{-1}) lies around 180 cm^{-1} to the red. In interpreting this observation we were helped by the work of Hickman *et al.* who were able to determine the vibrational frequencies of a few optically inaccessible states in both the S_0 and S_1 electronic states of toluene by populating levels via collisions with S_1 37^1 toluene.[19] In particular, they identified that the ν_{16} , an A' C-C stretching mode, as 407 cm^{-1} in the S_0 state and 228 cm^{-1} in S_1 . The 16_1^1 transition would thus lie $407 - 228 = 179\text{ cm}^{-1}$ to the red of the monomer 0_0^0 transition. This sequence transition has been observed in the two photon spectrum of room temperature toluene by Krogh-Jespersen *et al.*[21] Hence, we interpret the dispersed fluorescence spectrum following pumping of the toluene-Ne $\overline{37_0^1}$ transition as fluorescence arising from the monomer 16_1^1 and 0^0 levels (and possibly other levels, too). In other words, VP from the $\overline{37^1}$ level leaves toluene in S_1 16_1^1 and 0^0 levels. As it is optically inaccessible from the ground state, the fluorescence lifetime of the monomer S_1 16_1^1 level is unknown. In our previous work we extracted a lifetime of 74.7 ± 4.2 ns following pumping of the $\overline{37_0^1}$ transition in toluene-Ne which is

intermediate between the lifetimes of the monomer 37^1 level (70.7 ± 1.9 ns) and the monomer 0^0 level (85.7 ± 1.1 ns), consistent with this interpretation.

D. $\overline{11^1}$ SVLF spectra

In their comprehensive dispersed fluorescence study of the monomer, Hickman *et al.* inferred the onset of IVR in the S_1 state to be around $0^0 + 750$ cm^{-1} , based on the observation of a broad structureless feature in the spectra of all levels at and above this. Whilst almost all levels above this are characterised by broad unresolved dispersed fluorescence spectra, the spectrum of the monomer 11^1 level (as well as 10^1) does exhibit strong structure on a broad diffuse spectral background. In an attempt to investigate the effects of IVR on cluster dynamics we have recorded the SVLF spectra of complex levels built upon the monomer 11_0^1 transition (Figure 7). The spectra are considerably more congested than those from other levels supporting the view that fluorescence occurs from multiple vibronic states.

IV. Conclusions

The dispersed fluorescence spectra of several vibrational levels of S_1 toluene-Ar and toluene-Ne complexes have been reported. Comparison of the spectra with single vibronic level fluorescence spectra of toluene monomer levels confirms the importance of mode-selective vibrational predissociation and in some cases permits the identification of the toluene molecule final vibrational level. In at least one case, the result of VP is to leave the toluene in a level which is not observed in the fluorescence excitation spectrum. These studies help in the interpretation of anomalies in several cluster level fluorescence decay lifetimes reported previously.

FIGURE CAPTIONS

Figure 1

Fluorescence excitation spectrum of jet cooled toluene expanded in helium. The marked vibrational levels are those from which fluorescence has been dispersed in the corresponding toluene–RG complexes. Hickman *et al.* [19] identified the onset IVR around the $12^1/23^124^1$ Fermi resonance. Transition wavenumbers are shown relative to the S_1 – S_0 origin transition at 37477 cm^{-1} . Inset: expanded region of the same spectrum following expansion in Argon showing the presence of toluene–Ar peaks (*) red shifted from monomer transitions.

Figure 2

Schematic S_1 energy level diagram of toluene and toluene–RG complexes illustrating the relative positions of the levels important in this study. Arrows indicate principal vibrational predissociation pathways identified by dispersed fluorescence.

Figure 3

Dispersed spectra recorded following pumping of the vibrationless $S_1 \overline{0_0}$ levels of the toluene–Ne (upper graph) and toluene–Ar (lower graph) complexes. For comparison, the dispersed fluorescence spectra from the 0_0 level of toluene expanded in the same carrier gas are shown. The red-shift in the fluorescence from the cluster levels compared with the monomer is visible in each case. Asterisks mark the transitions possibly contaminated with pump radiation.

Figure 4

Single vibronic level fluorescence spectrum recorded following pumping of the $\overline{13_0^1/24_0^125_0^1}$ transition in the toluene–Ar complex. The spectrum bears little similarity to the spectrum from the $13^1/24^125^1$ level in the toluene monomer (upper graph) but matches well the spectrum of the monomer 0^0 level (lower graph). Asterisks mark the transitions possibly contaminated with pump radiation.

Figure 5

Single vibronic level fluorescence spectrum recorded following pumping of the $\overline{37_0^1}$ transition in the toluene–Ar complex. Again, the spectrum bears little similarity to the spectrum from the 37^1 level in

the toluene monomer (upper graph) but matches well the spectrum of the monomer 0^0 level (lower graph). Asterisks mark the transitions possibly contaminated with pump radiation.

Figure 6

Single vibronic level fluorescence spectrum recorded following pumping of the $\overline{37}_0^1$ transition in the toluene-Ne complex. The dispersed fluorescence spectrum is reminiscent of neither the corresponding monomer vibrational level nor the monomer 0^0 level. Instead the red-shift of the most prominent feature in the spectrum from the monomer 0^0 transition suggests the population of the toluene 16^1 level. Asterisks mark the transitions possibly contaminated with pump radiation.

Figure 7

Single vibronic level fluorescence spectrum recorded following pumping of the S_1 ν_{11} mode in the toluene monomer (top), the toluene-Ar complex (middle) and the toluene-Ne complex (bottom). ν_{11} lies above the threshold for IVR [19] and the spectra probably reflect fluorescence from a variety of vibrational levels. Asterisks mark the transitions possibly contaminated with pump radiation.

FIGURES

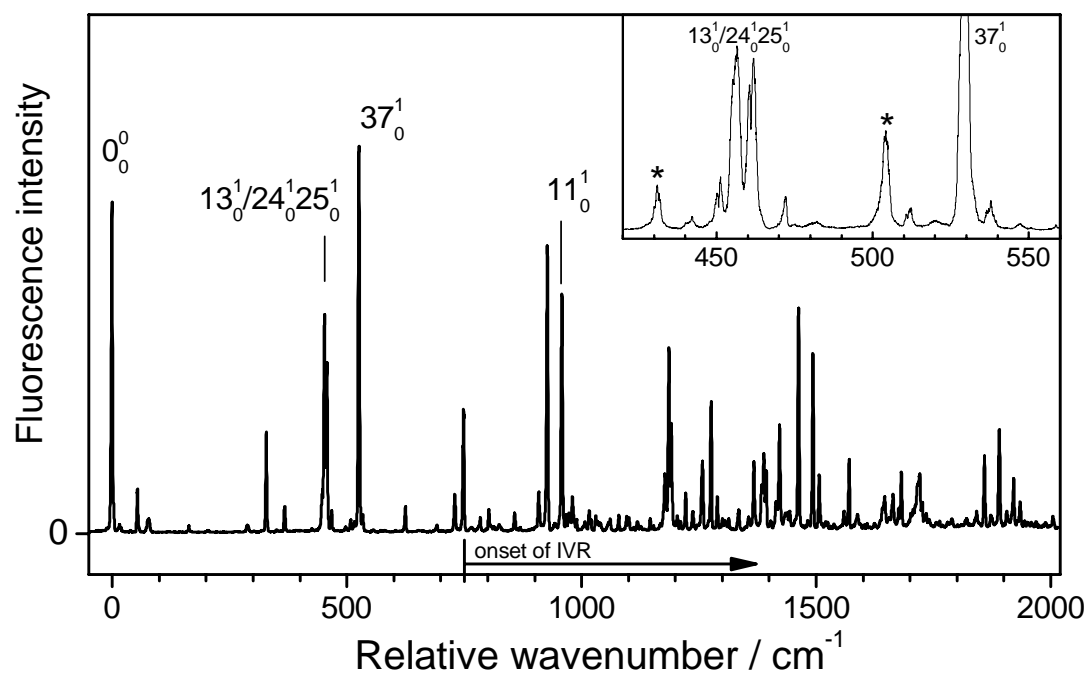


FIGURE 1

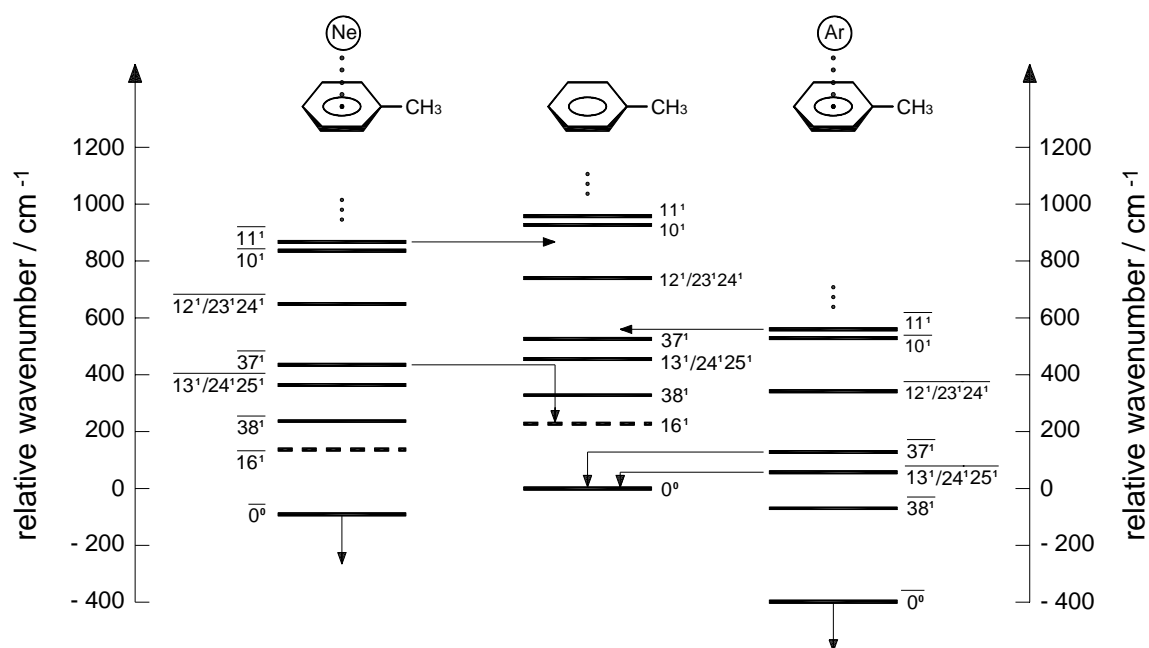


FIGURE 2

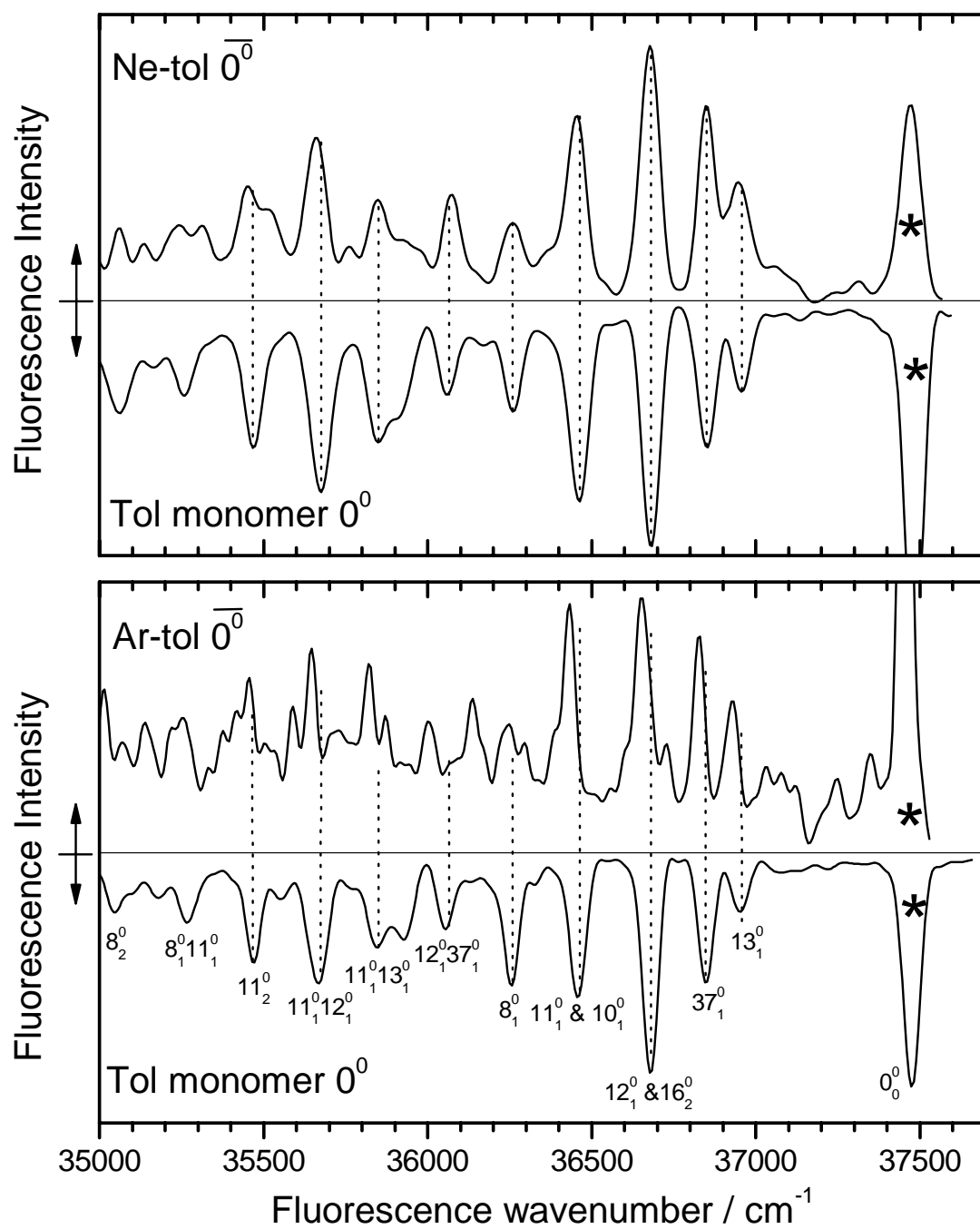


FIGURE 3

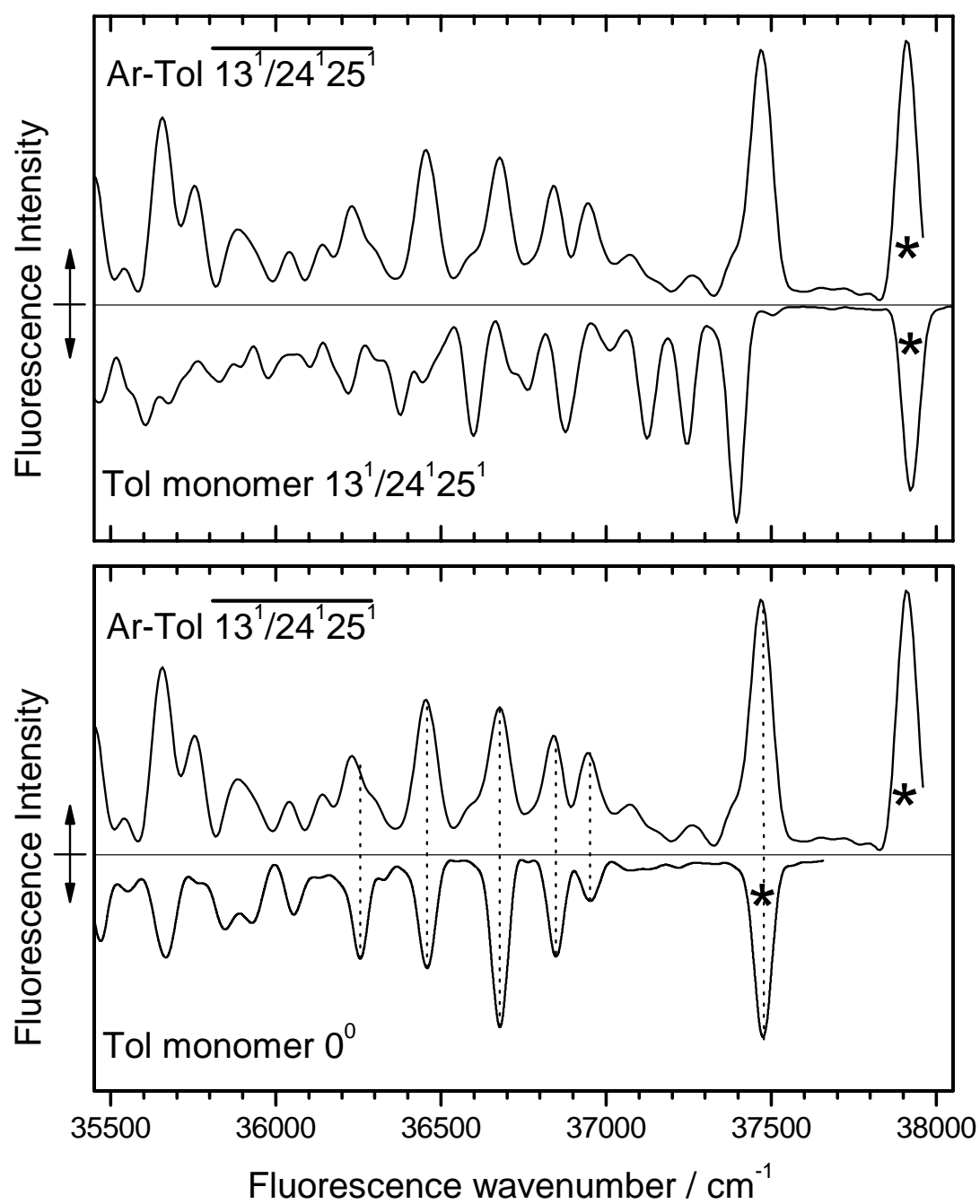


FIGURE 4

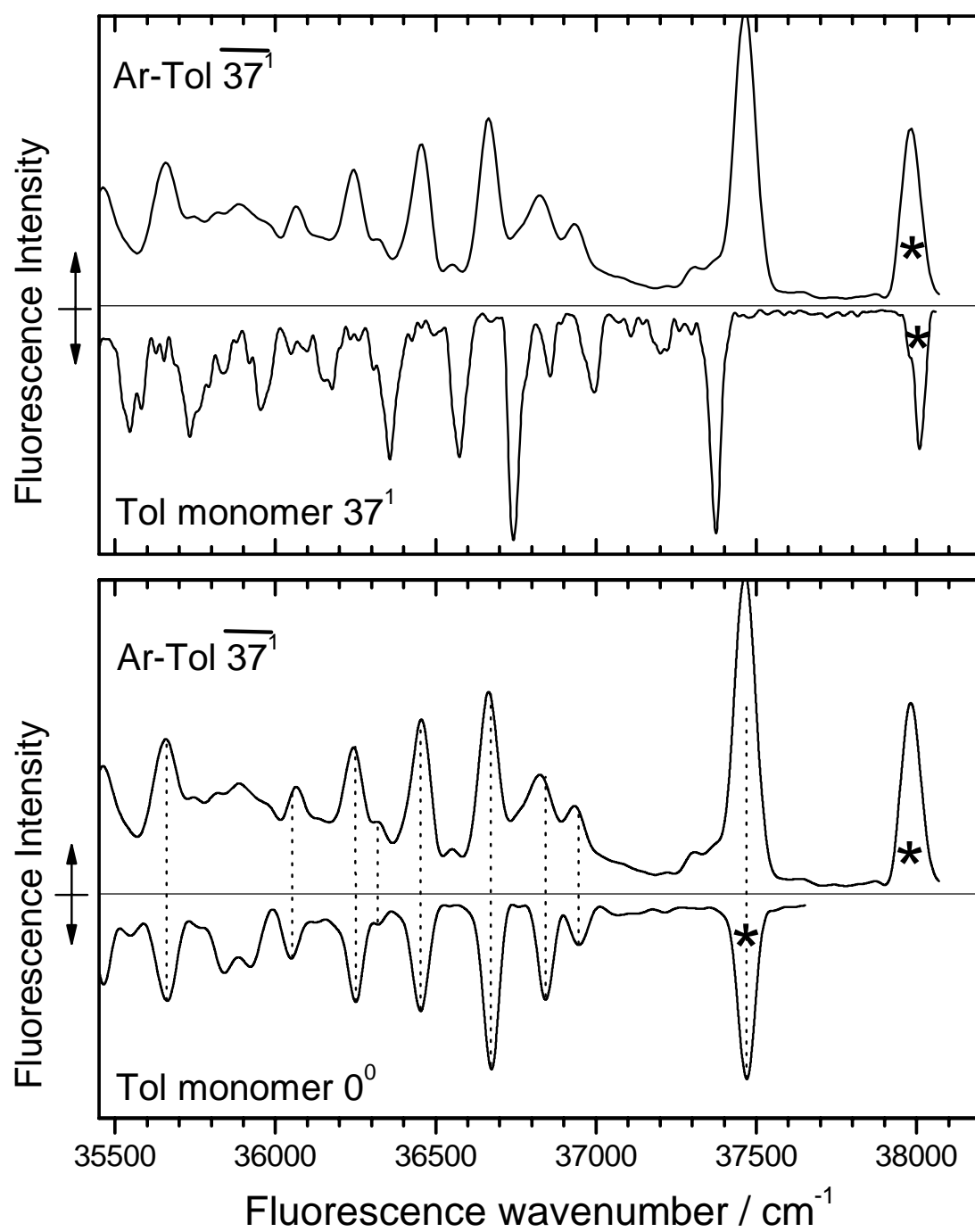


FIGURE 5

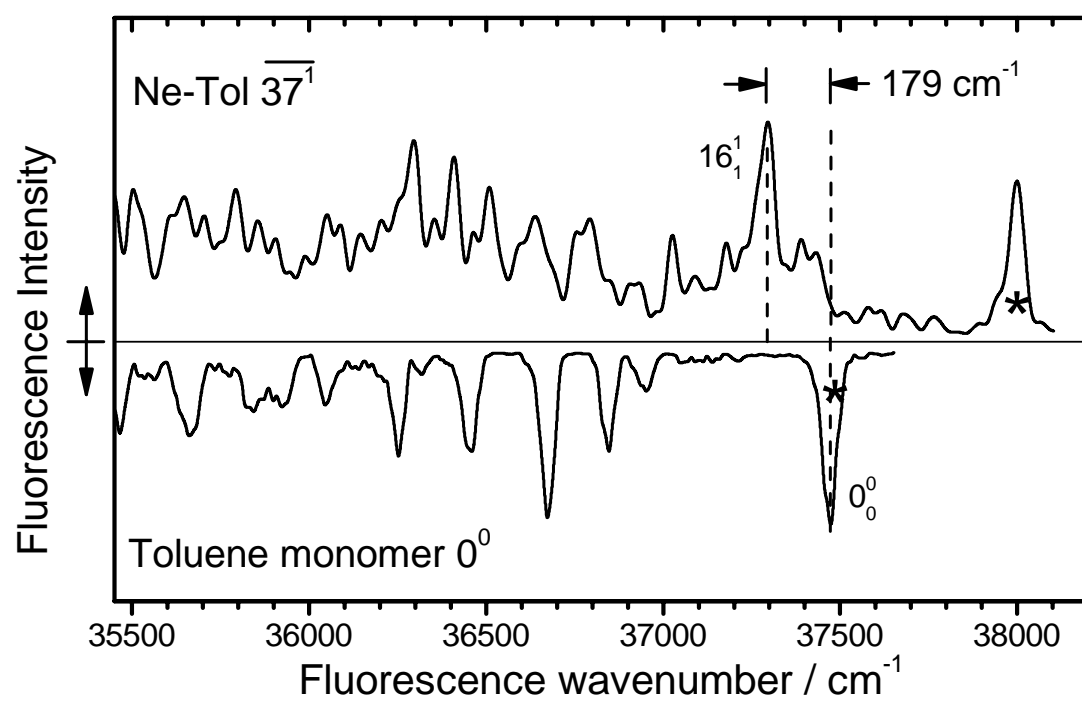


FIGURE 6

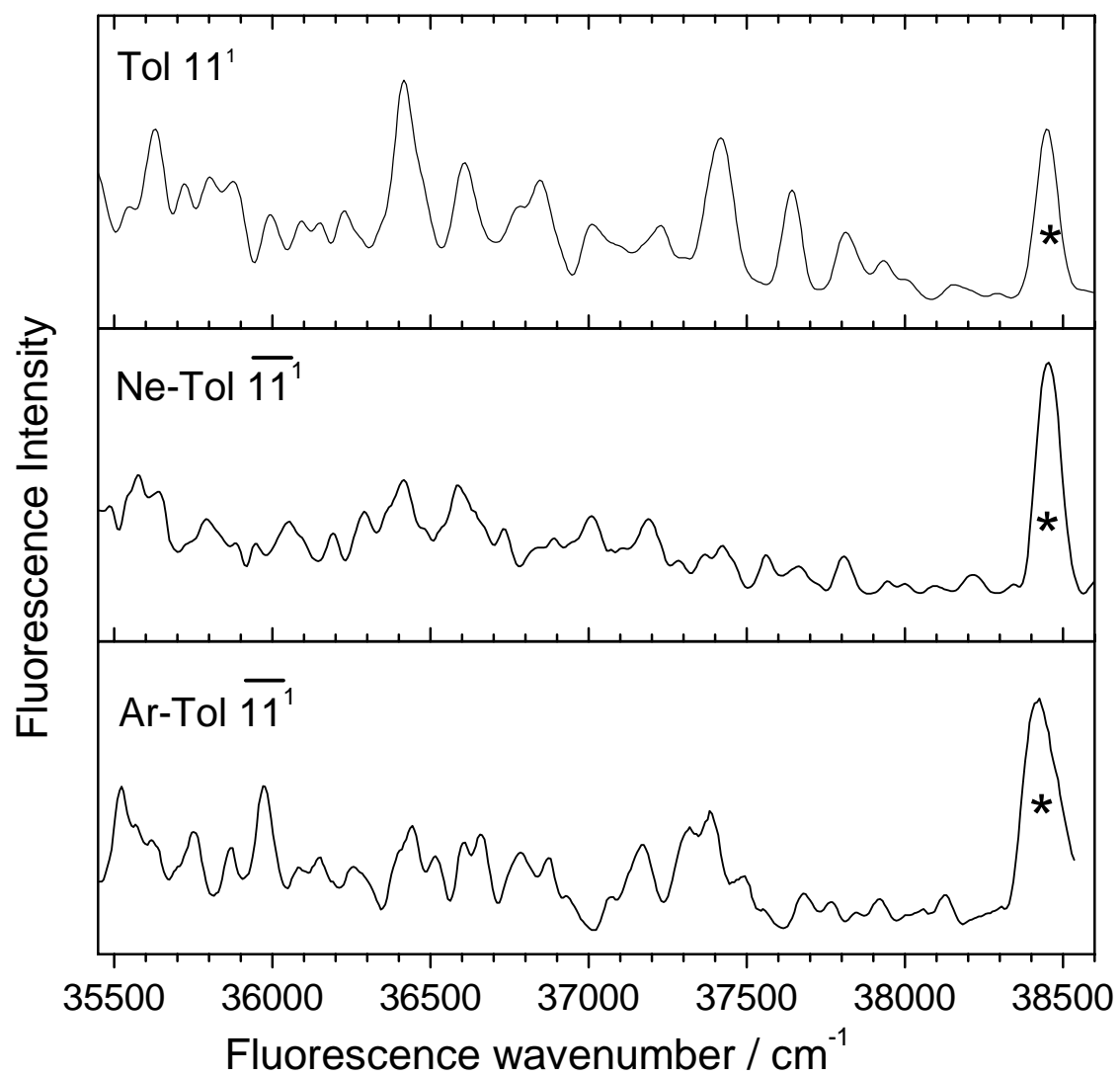


FIGURE 7

<i>Assignment</i>	<i>Lifetime (ns)</i>
Toluene 0_0^0	85.7 ± 1.1
Toluene-Ne $\overline{0_0^0}$	77.2 ± 2.6
Toluene-Ar $\overline{0_0^0}$	42.5 ± 2.0
Toluene 37^1	70.7 ± 1.9
Toluene – Ne $\overline{37^1}$	74.7 ± 4.2
Toluene – Ar $\overline{37^1}$	82.6 ± 2.2
Toluene $13^1 / 24^1 25^1$	69.2 ± 3.7
Toluene – Ne $\overline{13^1 / 24^1 25^1}$	Overlapped
Toluene – Ar $\overline{13^1 / 24^1 25^1}$	82.1 ± 0.8

TABLE 1: Fluorescence lifetimes observed following excitation of individual S_1 vibrational levels in toluene and toluene-Ar, Ne clusters (from [24])

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