

# Sharp Resonances in Radiationless Transitions

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We have observed extremely sharp Doppler-free resonances in the measurement of molecular lifetimes of excited states in the low pressure gas-phase of naphthalene. These resonances are seen at extremely low magnetic fields and have a width of only 3 Gauss. Their extreme sharpness of  $2.8 \times 10^{-4} \text{ cm}^{-1}$  is within a factor of 2 of the natural width of the radiationless transition, and some 130 fold below the Doppler width of the state considered. Such sharp resonances should provide unique insights into the states and dynamics of radiationless processes. They are probably due to sharp field dependent changes in the non-radiative coupling strength of the spin-orbit transition into the triplet.

We have launched a new series of magnetic experiments. We excited a portion of a molecular vibronic state of naphthalene with a sharp tunable laser ( $\Delta\lambda = 0.27 \text{ cm}^{-1}$ ) near the origin of the  $8(b_{1g})$  vibronic band with a short pulse and measured the lifetime. We then applied a weak magnetic field and measured the fluorescence decay in the field as a function of field strength (up to about 100 Gauss). This  $8(b_{1g})$  band is at an excess energy of  $438 \text{ cm}^{-1}$  ( $p = 70 \text{ mTorr}$ ); the lifetime is about 265 nsec. As the field is increased the lifetime remains constant, until near 20 Gauss a strong decrease in the lifetime is observed. Such sharp shortenings in the lifetime seem to occur at very discrete magnetic field strengths only. As can be seen in Fig. 1, the novel sharp resonances in the lifetime are only 3 Gauss wide and spaced about 30 Gauss apart. The maxi-

mum field of 114 Gauss is well below that which produces significant mixing of spin polarizations. The observed 3 Gauss resonances correspond to a width of  $2.8 \times 10^{-4} \text{ cm}^{-1}$ , which is extremely narrow, far below the Doppler width for this system ( $3.7 \times 10^{-2} \text{ cm}^{-1}$ ) and much sharper than the excitation bandwidth of  $0.27 \text{ cm}^{-1}$ . Taking the measured lifetime as 265 nsec, we obtain a natural width of  $1.3 \times 10^{-4} \text{ cm}^{-1}$  for the state. This value is close to that observed in the resonances. Hence these resonances have essentially the natural width of the states involved and could be used as a direct measure for lifetimes of radiationless process.

Measurements at the electronic origin of the  $S_1$  state show resonances which have a similar spacing. The resonances in the  $7(b_{1g})$  mode ( $0 + 911 \text{ cm}^{-1}$ ) have a spectrum which is somewhat more dense. For the  $8(b_{1g})$  band the quantum yields were also measured simultaneously with the lifetimes, over the resonances of the field scan. The tracking of the lifetime by the quantum yield is within 2%. Since the quantum yield is given by  $\Phi = \tau_{\text{obs}}/\tau_{\text{rad}}$  this means that the radiative lifetime is constant over these resonances. This indicates that these new resonances appear to be due solely to a radiationless process.

The above preliminary results show that we are confronted with extremely sharp resonances in a lifetime spectrum at very low fields. A reasonable mechanism for such resonances could be sought in the Zeeman sensitivity of the levels in the triplet state. It should be emphasized that these are resonances in lifetimes and not only in intensity and hence are qualitatively different from level crossing and other coherent experiments. In fact we have carried out experiments in which the magnetic field is both parallel and perpendicular to the linear polarization vector of the laser. These experiments reveal essentially the same structure.

Several hundred rotational states are excited by the  $0.27 \text{ cm}^{-1}$  excitation bandwidth. These states are spaced an average of  $2 \text{ cm}^{-1}$  apart. Since this is about 200 times larger than the width of the observed resonances one may conclude that the rotational states form a discrete manifold and are not coupled in this experiment. The discreteness of these resonances doubtless means that but a few triplet levels of the possible  $10^{11}$  vibronic levels/ $\text{cm}^{-1}$  (if  $T_1$  is involved) can accept the energy, due to electronic and Franck-Condon restrictions. Indeed, this number is effectively lowered to  $10^5$  vibronic levels/ $\text{cm}^{-1}$  by virtue of non-totally symmetric vibrational overlap-integral selection rules alone.

We consider that discrete rotational levels are brought to interact with a discrete triplet ro-vibronic level by an energy shift induced by a precise value

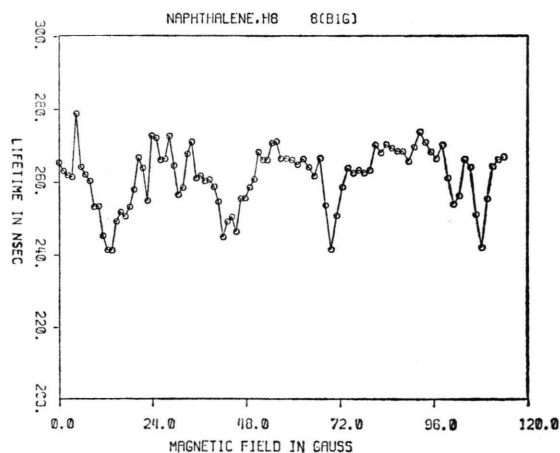


Fig. 1. Magnetic field dependence of the observed lifetime of naphthalene,  $h_8$  excited at  $32454.6 \text{ cm}^{-1}$ .



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of the magnetic field. Hence, even though many levels are contained within the excitation bandwidth, nevertheless the resonances can be sharp; in fact, here they are some three orders of magnitude sharper than the excitation bandwidth. This alone distinguishes these resonances from typical sharp resonances in a radiation field in which the magnitudes of the resonance and excitation linewidths must be comparable. Most interesting is the fact that these are resonances in a radiationless transition whereas most other sharp resonances involve radiative transitions, i. e. dipole operators in radiation fields. This adds intrinsic interest to these new very sharp resonances.

In conclusion, we have observed extremely sharp resonances at very low magnetic fields in a radiationless process, and this in a large molecule, naphthalene, in the dilute gas-phase. The sharp resonances are typically  $2.8 \times 10^{-4} \text{ cm}^{-1}$  wide and are more than two orders of magnitude narrower than the Doppler width, indeed far narrower than the excitation bandwidth and are apparently limited only by the natural lifetime of the radiationless process. The mechanism is presumed to be one of resonant tuning of the sharp singlet and triplet levels by the magnetic field. These resonances provide direct information about the final levels of a radiationless, non-optical transition.