Magnetic Field Dependence of Molecular Quantum Beat: Biacetyl

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The effect of an external magnetic field on the decay of an excited single rotational state of the ^1A_u electronic state of biacetyl is observed in a hypersonic jet experiment after narrow bandwidth laser excitation. The lifetime of the excited state decreases already at low magnetic fields and the molecular quantum beat vanishes.

Biacetyl at room temperature shows a broad nearly unstructured absorption spectrum which is due to sequence congestion which arises from the low rotational constants of the molecule and from the internal rotation of the methyl groups [1]. Furthermore, the decay of the fluorescence from the excited S_1 state shows a biexponential behavior even at zero pressure, which consists of a fast and a slow part with the decay constants $8 \cdot 10^7$ sec^{-1} and $2 \cdot 10^4$ sec^{-1}, respectively [2]. The decay behavior was the subject of many theoretical treatments [2, 3, 4], but the biexponential decay could not yet be unequivocally explained. This is due to the lack of a method to prepare a single rotational state; therefore the emission always consisted of the superposition of the decay of many excited states. Spectral congestion, however, can be overcome by the technique of isentropic expansion in a hypersonic jet. Here the molecules are seeded into a carrier gas and expanded into the vacuum. During the expansion the internal temperature of the molecule is lowered to a few degrees Kelvin whereas the molecule is still isolated in the gas phase [5]. This technique reduces the rotational transitions to a few lines, and single rotational states can be prepared. As there are no further collisions after the expansion, the decay can be studied under nearly collision free conditions [6].

When biacetyl is seeded into a hypersonic jet and a single rotational state is excited, a decay behavior different from the biexponential decay of the bulb experiment is observed. The decay has been shown, for many rotational states, to be modulated by molecular quantum beats [7]. This molecular quantum beat arises from the coupling to a second state, which possesses no oscillator strength. In the case of biacetyl this is postulated to be the triplet state T_1. Such a triplet state should be magnetically sensitive, and therefore one might expect an effect of an external magnetic field on the molecular quantum beats.

In our experiment we expanded a mixture of a few Torr of biacetyl in Helium at a pressure of 4.9 atmospheres through a pulsed nozzle of 0.2 mm diameter into a vacuum chamber with a background pressure of about 10 millitorr. Excitation occurred with a pulsed dye laser of 8 nsec duration and 0.2 cm^{-1} bandwidth, which crossed the hypersonic jet at 15 mm from the nozzle. Built into the vacuum chamber there was also a pair of Helmholtz coils, which could provide a magnetic field up to 40 Gauss at the interaction region. The decay was monitored with a fast photomultiplier and averaged over several hundred laser shots for every decay curve.

Figure 1a shows the molecular quantum beat of biacetyl for zero magnetic field. The overall decay constant is $0.9 \cdot 10^6$ sec^{-1}, which is in between the values for the slow and fast decay at room rempera-ture.

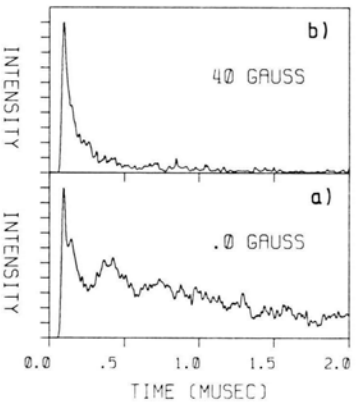

Fig. 1. Magnetic field effect on the fluorescence decay of biacetyl. a) Quantum beat at zero magnetic field, b) fluorescence quenching at 40 Gauss.

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Superimposed on the decay there is a quantum beat with a frequency of 3.5 MHz. If one now applies a magnetic field, the decay rate increases and the beat becomes less pronounced. At a magnetic field of 40 Gauss the beat can no longer be detected (Figure 1 b).

The dependence of the lifetime versus the magnetic field is shown in Figure 2. The lifetimes are determined from a least squares fit starting 200 nsec after excitation to minimize effects from the stray light or emission from background gas. Even for weak fields the effect of the magnetic field on the lifetime is very strong and decreases linearly with the magnetic field within the range of 40 Gauss. The magnetic quenching shows no limiting behavior as found in the case of the magnetic quenching of glyoxal [8], which saturates at 400 Gauss. It is also interesting to note that the magnetic field for the most part influences just the decay time of the system but does not affect the interaction which leads to the quantum beats.

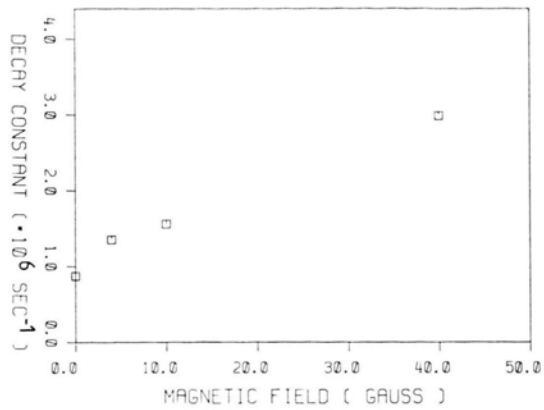

Fig. 2. Magnetic field dependence of fluorescence quenching of biacetyl.

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