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THE BIG BANG AND ELEMENT CREATION

A DISCUSSION ORGANIZED AND EDITED BY
D. LYNDEN-BELL, F.R.S.

(Discussion held 11 and 12 March 1982 – Typescripts received 18 May 1982)

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Molecular spectroscopy and dynamics below the Doppler width

BY E. W. SCHLAG, H. L. SELZLE, W. HENKE, E. RIEDLE AND H. J. NEUSSER

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The density of states in polyatomic molecules is so high that many spectroscopic transitions are only observed as large groupings even in high-resolution spectroscopy. This is due to the fact that many of these states are buried beneath the Doppler width of the optical transition. We here discuss new sub-Doppler experiments for optical transitions in molecular spectra.

For benzene we have obtained a resolution of less than 80 MHz, more than one order of magnitude below Doppler width. From these measurements precise rotational constants of the excited state are reported for the first time. Doppler-free experiments were also performed with biacetyl when measuring the molecular quantum beat in the decay after fluorescence excitation in a supersonic jet. This technique permits the spectroscopy of nearby coupled states well below the Doppler limit and also below the bandwidth of the excitation laser.

Recent advances in experimental technology allow sub-Doppler measurements to be extended to the régime of small and medium size molecules. The methods that can be used are two-photon spectroscopy (Biraben *et al.* 1974; Levenson & Bloembergen 1974), level-crossing spectroscopy (Bonilla & Demtröder 1978), and molecular beam experiments including supersonic jets and quantum beats (Levy 1980).

These methods are extremely important because the density of levels in the excited states of molecules is large, and many transitions therefore lie within the Doppler width. This is particularly so for rotational transitions and spectra of polyatomic molecules that only produce rotational envelopes, where the rotational fine structure is hidden behind the Doppler profile of the transition. In addition, one cannot study the splitting of energy levels arising from interactions between different electronic manifolds when the coupling matrix element is less than the Doppler width of the observed transitions. We have applied Doppler-free two-photon excitation with narrow-bandwidth lasers of large molecules to obtain rotationally resolved spectra from which structural information can be obtained with an accuracy hitherto impossible (Riedle *et al.* 1981). We have also achieved Doppler-free experiments even with broad bandwidth pulse excitation for molecular quantum beats (Henke *et al.* 1981). In this case the observed beat frequency in the decay of the fluorescence is determined only by the level spacing and the coupling of the levels in an individual molecule and is therefore not affected by the thermal velocity distribution of the ensemble. The total half bandwidth due to Doppler broadening is given by (Selzle *et al.* 1981)

$$\Delta\omega_D = 7.163 \times 10^{-7} \sqrt{(T/M)} \omega_0,$$

and the limiting conditions for the case of separation of two lines is given in figure 1. As is shown, cooling in a supersonic jet reduces the Doppler broadening substantially but is still not sufficient to resolve single rotational lines for large molecules.

[47]

A comparison between transition line intervals, natural line width and Doppler width is given in table 1. As can be seen for benzene and biacetyl the average distance between lines is larger than or similar to the natural line width but smaller than the Doppler width; separation of lines can therefore be achieved with Doppler-free methods. For still larger molecules like anthracene, the line separation becomes smaller than the natural line width and line separation will therefore be impossible.

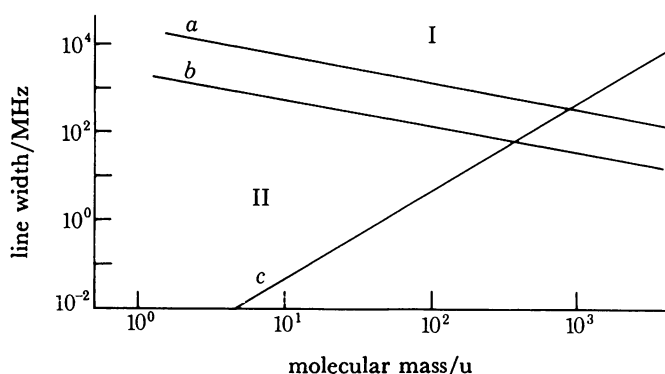


FIGURE 1. Comparison between Doppler limit and line width of a transition: (a) Doppler width at room temperature (300 K); (b) Doppler width in jet (3 K). I, separation of lines is possible for Doppler-limited methods if the line spacing is larger than the line width; II, separation of lines is only possible for Doppler-free methods and a line spacing larger than the Doppler-free line width. The curve for the non-radiative width (c) is an estimate for $k_{\text{non-rad}} \propto \rho$, where ρ is increasing with the mass of the molecule.

TABLE 1

	molecular mass/u	number of atoms	number of vibrations	rotational constants cm^{-1}	average distance between transitions MHz	Doppler width MHz	natural line width MHz
hydrogen, H_2	2	2	1	20.01	1 200 000	9 500	
formaldehyde, H_2CO	30	4	6	8.75, 1.12, 1.01	3 000	1 700	0.5
benzene, C_6H_6	78	12	30	0.189, 0.189, 0.0945	200	1 500	6
biacetyl, $\text{C}_4\text{H}_6\text{O}_2$	86	12	30	0.176, 0.105, 0.0675	20	750	36/0.15
anthracene, $\text{C}_{14}\text{H}_{10}$	178	24	60	0.074, 0.016, 0.014	< 1	680	60
large molecule, $\text{C}_{75}\text{H}_{100}$	1000	175	519	0.01, 0.002, 0.001	$\ll 1$	400	500

In our experiment we applied Doppler-free two-photon absorption to overcome the Doppler broadening in the spectrum of the benzene molecule. It was possible to resolve as many as 400 individual rotational transitions for a polyatomic molecule as large as benzene. Levels up to $J \approx 30$ were seen in a spectrum extending over more than 100 GHz with a resolution of about 80 MHz. The two-photon spectrum of the benzene molecule is obtained in a sub-Doppler two-laser experiment (Riedle *et al.* 1981). One laser is a Coherent 559 continuous-wave (c.w.) single-mode dye laser using Coumarin 102 dye and emits around 494.3 nm. The second is a high-power c.w. Ar^+ laser providing the second photon of fixed wavelength for the two-photon process. The high power of the second laser is necessary because of the low cross section of a two-photon transition where in addition the oscillator strength is distributed over many rovibronic lines.

The two counterpropagating laser beams are carefully aligned in a common focus in a low-pressure gas cell. Ultraviolet fluorescence is monitored and by scanning the dye laser the sub-

Doppler spectrum is measured. This spectrum and the corresponding Doppler-limited spectrum, which can be achieved by conventional methods, are shown in figure 2. This reflects the extremely well resolved Q-branch of the strongest vibrationally induced $(14_0^1)S_1 \leftarrow S_0$ transition. This high-resolution spectrum now allows the rotational analysis of this transition. For a perfect planar oblate symmetric top the transition frequency for $\Delta J = 0$, $\Delta K = 0$ is given by

$$\Delta E = (B'' - B') [J(J+1) - \frac{1}{2}K^2],$$

with

$$A'' = B'' = 2C'' \quad \text{and} \quad A' = B' = 2C'$$

respectively and the planarity condition $I_C - I_A - I_B = 0$ is fulfilled. The measured spectra now can be compared with theoretical absorption spectra and from the known high-precision rotational constants of the ground state (Jensen & Brodersen 1979) one can determine the

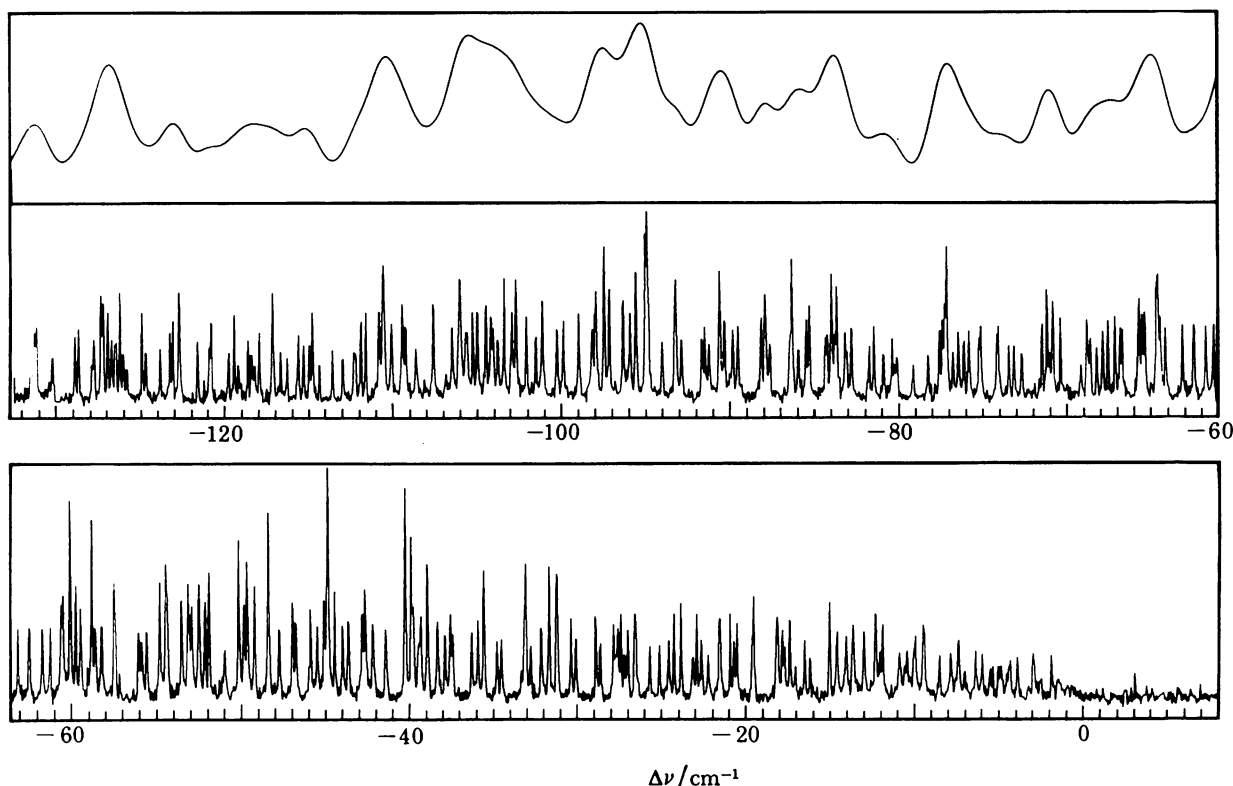


FIGURE 2. Doppler-free two-photon absorption spectrum of benzene: $\Delta J = 0$; $\bar{\nu} = 39657 \text{ cm}^{-1}$. The upper trace represents the corresponding Doppler-limited spectrum.

rotational constants for the excited state. From the comparison of the computed spectrum one sees that some lines that should coincide are split, for instance the transitions for $J, K = 9, 4$ and $J, K = 11, 10$. From the splitting of 0.19 GHz for these lines and similar splittings for other lines one can deduce that the simple energy relation for the planar symmetric rotor is no longer valid. Two possible effects can now modify the J or K dependence, or both, and would explain the line splitting. The first would be centrifugal distortion, but an estimate shows that this effect would be more than one order of magnitude smaller than our observed result.

The second explanation would be that the assumption $2C' = B'$ is not correct so that there is an inertial defect ($I_C - I_B - I_A \neq 0$). If one now assumed that the benzene is perfectly

symmetric in the ground state the fit also demands a perfect symmetric top in the excited state 14^1 . The inertial defect then shows that the effective molecular structure is no longer planar, with an effective distance of the carbon atoms of ± 2.1 pm from the original molecular plane. This is the first time that individual rotational transitions have been uncovered far underneath the Doppler profile in the electronic spectrum of a polyatomic system, thus revealing structural information that was not possible until now.

A second very important method to reach below the Doppler width is quantum beat spectroscopy (Chaiken *et al.* 1979). This method can be applied for the spectroscopy of the interaction of nearly degenerate states in a molecule, which are coupled by an interaction like spin-orbit coupling. From this coupling, level-anticrossing will arise, which repels the coupled levels. The quantum beats are then a direct measurement of the microscopic coupling elements. This technique therefore permits horizontal spectroscopy, i.e. an isoenergetic transition between two different electronic states in an isolated molecule. We have now applied this method to the study of biacetyl in a supersonic jet (Selzle *et al.* 1981).

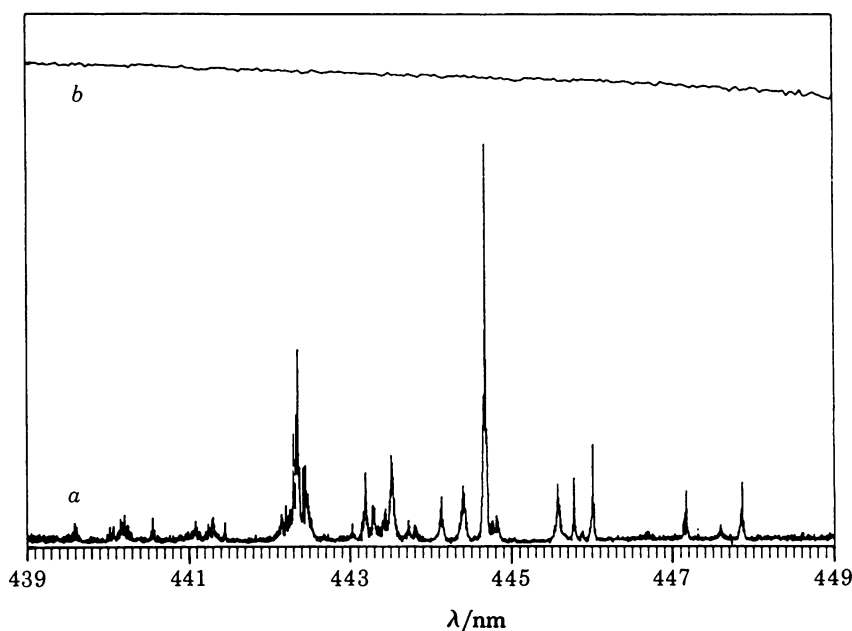


FIGURE 3. Jet spectrum of biacetyl: (a) fluorescence excitation spectrum in a supersonic jet; (b) fluorescence excitation spectrum at room temperature.

The spectrum of biacetyl at room temperature is so dense because of rotational congestion that one cannot achieve any rotational resolution. Therefore one has to cool the molecule in a supersonic jet to reduce line density, as shown in figure 3. The fit of the rotational transitions gave an effective rotational temperature of *ca.* 1 K at a He-carrier pressure of 4.9 atm (*ca.* 500 kPa), when expanding through a nozzle of 0.2 mm diameter into a vacuum. The molecules are excited with a narrow bandwidth (0.05 cm^{-1}) pulsed dye laser, and the fluorescence emission is detected.

If one excites a single rotational transition an interesting effect is observed in the emission. The fluorescence decay is no longer single-exponential but shows a regular beat pattern, which is shown in figure 4. This molecular quantum beat arises from coupling of the single vibronic level in S_1 with a second 'dark' state which in biacetyl is preferably a triplet state. This decay

behaviour now can be fitted with a density matrix calculation that solves the Liouville equation for a coupled two-level system (Haberkorn *et al.* 1980):

$$d\hat{\rho}/dt = -i\hat{L}_0\hat{\rho} - i\hat{L}'\hat{\rho} - \Gamma\hat{\rho},$$

where $\hat{\rho}$ is the density matrix for the two levels, \hat{L}_0 is the Liouville operator for the basis set chosen, \hat{L}' describes the interaction of the anticrossing levels and Γ is the damping operator, which describes the decay and the dephasing of the levels. The result of this calculation is also shown in figure 4. This intramolecular process can now interfere with perturbations from collision with other molecules or external fields.

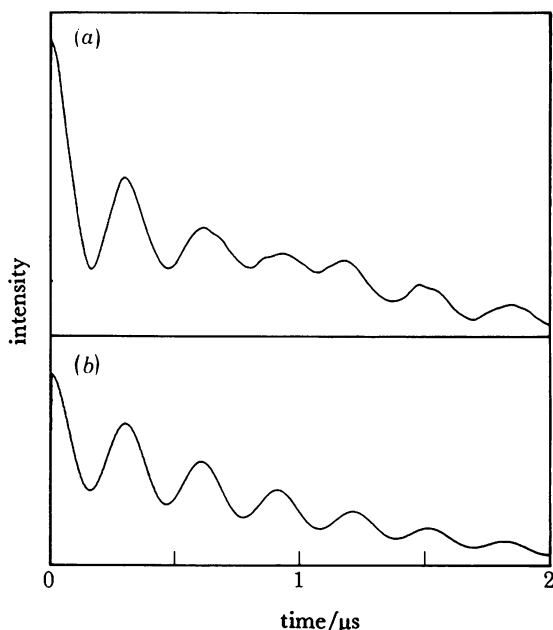


FIGURE 4. Quantum beat in biacetyl: (a) fluorescence decay after narrow-bandwidth pulse excitation of a single rotational line; (b) calculated decay curve for a coupled two level system.

TABLE 2. QUANTUM BEAT PARAMETERS

parameter†	$H = 0 \text{ G}‡$	$H = 4 \text{ G}$
H_{mn}	1.11 MHz	1.11 MHz
W_{mn}	2.46 MHz	2.37 MHz
decay	0.5 MHz	0.8 MHz
dephasing	1.40 MHz	2.66 MHz

† H_{mn} , interaction between the coupled states; W_{mn} , level separation without interaction; decay, overall decay constant; dephasing, pure dephasing constant.

‡ $1 \text{ G} = 10^{-4} \text{ T}$.

Collisions can be classified as inelastic collisions, which relax the population of the states and are detected by shortening the observed mean lifetimes, and collisions that only change the phase of the coupled states. The latter can be detected with the Doppler-free method because they wash out the beat pattern. This is a unique method for determining the cross section for a phase-changing collision, which otherwise could only be measured with very sophisticated line shape measurements. The observed quantum beat parameters are given in table 2, where the pure dephasing most probably arises from residual collisions.

For a coupling to a triplet manifold, which is a possible interaction in biacetyl, the quantum beat should be affected by an external magnetic field interacting with the coupled triplet state (Henke *et al.* 1980). The experimental results obtained by applying a weak magnetic field are shown in figure 5. The magnetic field acts in two different ways on the decay of the excited state. First one sees a quenching of the slow part of the fluorescence decay like the quenching also observed in glyoxal, only in this case a much smaller field is needed. The other feature is a change in the beat pattern. The beat frequency in this case becomes smaller, which indicates a level shift between the interacting states and can be interpreted as a Zeeman level shift of the triplet state. There is also an increase in the dephasing due to the magnetic field. From these measurements all parameters for the coupling of states with separation below the Doppler width can be derived.

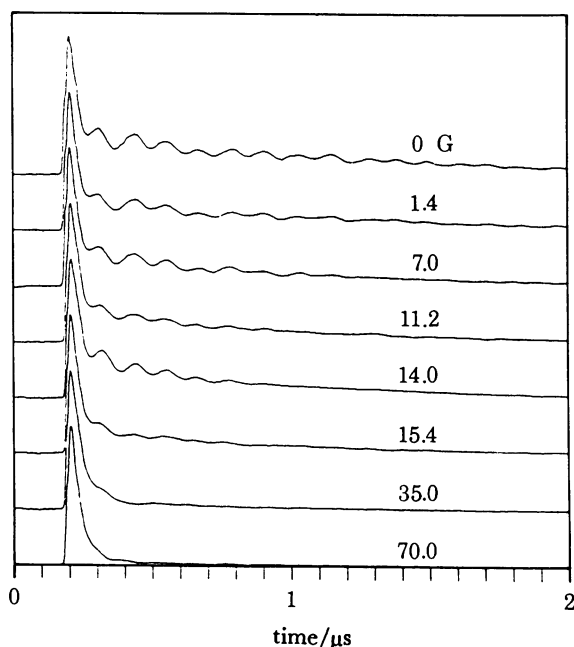


FIGURE 5. Effect of magnetic field on the fluorescence decay of biacetyl. With increasing field the slow component, which shows the quantum beat, is quenched.

In summary, one can say that with state-of-the-art narrow-band lasers, sub-Doppler experiments can be performed. With Doppler-free two-photon excitation, the rotational structure and hence the molecular structure of polyatomic molecules like benzene can be obtained. With quantum beats this sub-Doppler method allows horizontal spectroscopy between near-lying coupled states and in addition gives information about the type of interaction and coupling parameters.

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Discussion

B. A. THRUSH, F.R.S. (*Department of Physical Chemistry, University of Cambridge, U.K.*). The quantum beats observed in biacetyl are strongly affected by weak magnetic fields. Could Professor Schlag's observations be affected by stray magnetic fields generated by, for instance, the laser power supply?

G. W. SERIES, F.R.S. (*University of Reading, U.K.*). Professor Thrush has spoken of stray magnetic fields that may be present from a variety of sources. In my experience it is important not to overlook the stray field in the laboratory oscillating at the frequency of the a.c. mains. This is typically a few milligauss in amplitude.

E. W. SCHLAG. A d.c. magnetic field due to the magnetic valve of the pulsed jet nozzle was measured and found to be 40 mG. No a.c. field due to the magnetic valve was detected at the position of the interaction volume. However, an a.c. field oscillating at line frequency was found to be 4 mG. Therefore all stray fields are less than the Earth's magnetic field and can be neglected.