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An insert for single-molecule magnetic-resonance spectroscopy in an external magnetic field

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We describe an insert for optical and magnetic-resonance experiments on single molecules in a solid matrix at liquid-helium temperatures. The experimental arrangement allows *in situ* adjustment of the focusing lens and of the sample. A parabolic mirror serves to collect the fluorescence emission and to direct the light onto a photodetector. Microwaves can be irradiated through a coil around the sample while a superconducting magnet provides the possibility of a stationary magnetic field.

I. INTRODUCTION

In the past few years there has been a growing interest in the spectroscopy of individual molecules in the condensed phase.[1–3] In these experiments the following steps can be distinguished. First one incorporates impurity molecules at low concentration in a thin layer of a crystalline or glassy host matrix. Then by irradiating a tiny spot, with a tightly focused laser beam or by using a pinhole or an optical fiber, a small number of impurity molecules is excited from the ground state to the first excited state. A single molecule is selected by tuning the single-mode laser to the wing of the inhomogeneously broadened absorption band, where the density of absorbers is low. The detection of the single molecule occurs by monitoring its fluorescence emission. The experiment is usually performed at liquid-helium temperatures where the homogeneous linewidth of the individual absorbers is large compared to the overall linewidth of the absorption band.

Several experimental arrangements for performing optical spectroscopy on single molecules have been reported.[4–7] Here we describe a cryogenic insert which allows single-molecule magnetic-resonance experiments in zero field as well as in the presence of a magnetic field. The essential features of this design are: (a) the possibility to adjust the focusing lens in the excitation light path, (b) the possibility to adjust the position of the sample, (c) a coil to create the microwave magnetic field around the sample, (d) a superconducting coil to provide the static magnetic field, (e) a parabolic mirror to direct the emitted light to the photodetector.

II. THE EXPERIMENTAL ARRANGEMENT

The principle of the design of the insert is presented in Fig. 1(a). It is based on the structure described by Ambrose *et al.*[4] The adjustable lens L is used to focus the laser beam onto the sample S. The sample with a thickness of typically 10 μm, is laid on a LiF substrate without using glue so as to prevent mechanical stress. For protection, the sample is covered with a thin (100 μm) suprasil plate C. This cover is held in place by three dots of vacuum grease. The set consisting of the LiF substrate, the sample, and the suprasil cover is positioned such that the irradiated volume of the sample is in the simultaneous focus of the lens L and the parabolic mirror P. This mirror serves to direct the light emitted by the sample to the photodetector. The transmitted laser light is absorbed by the beam block B. In Fig. 1(b) the polygonal structure S in the center represents the sample. The small open circles indicate the three dots of vacuum grease. The small strip represents the region that can be accessed by the excitation light (*vide infra*). Close to the sample a small spot of aluminum (filled dot) serves as a tiny mirror allowing autocollimation of the excitation light.

The insert allows two mechanical adjustments at liquid-helium temperature. The first concerns the movement of the lens L along the x axis to optimize the focusing of the laser beam on the sample S. The second permits the movement of the sample S along the y axis, i.e., in a direction perpendicular to the laser beam. An important consideration underlying this design is the requirement that the use of a magnetomechanical adjustment, as described by Ambrose *et al.*,[4] is excluded. A permanent magnet, as used in their construction, would exert unacceptable forces on the insert in the presence of a magnetic field and moreover the stray field would spoil the zero-field magnetic-resonance experiments. To achieve the necessary movements of the lens and the substrate a brass construction was designed which can be tilted around a solid hinge by taking advantage of the elasticity of the metal. The attraction of this design is that it offers the possibility to make translations free of any backlash.

In Fig. 2(a) the principle of the movement of the LiF substrate, in a direction perpendicular to the laser beam, is explained. In Fig. 2(a) this direction is defined as the y axis. The z axis is parallel to the long axis of the cryostat and the x axis is parallel to the laser beam. The LiF substrate is mounted on a frame which has two holes in its lower part, one of which is marked by A. These holes are made to accommodate two pins connected to the structure D. The rotation of the screw E, which is in contact with the ball-shaped part F, induces a pivoting motion of the arm D around the hinge H_1. This hinge is a thinned part of the whole structure and the elasticity of the brass material supplies the necessary flexibility. The pivoting motion is translated into a nearly horizontal motion of the LiF substrate along the y axis. The rotation of the screw E is controlled by a worm wheel W_1

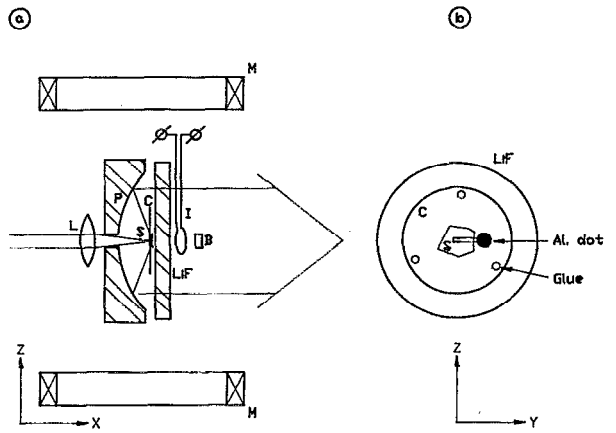

FIG. 1. (a) A simplified representation of a section of the insert in the $x-z$ plane. L is the focusing lens ($f=10$ mm), P the parabolic mirror ($f=5$ mm), S the sample, LiF the substrate, C the suprasil cover plate, and B is the beam block. M indicates the superconducting magnet which is mounted in a Helmholtz configuration with the magnetic field along the z axis. (b) A view of the sample mounting assembly along the x axis. The large inner circle indicates the suprasil cover plate. The three, small, open circles refer to the dots of vacuum grease which glue the cover plate to the LiF substrate. The black dot represents the aluminum mirror used in the autocollimation procedure. The horizontal strip indicates the area accessible by the laser focus.

which is connected to a knob at the top of the cryostat. The whole construction allows a horizontal displacement of the sample over 2 mm with a resolution of 4 μm. Because the focus on the sample can be moved in the z direction over 100 μm, by tilting the collimated laser beam in the same way as described by Ambrose *et al.*,[4] a total surface of 100×2000 μm^2 on the sample becomes accessible.

The principle of the adjustment of the focusing lens L is the same as for the displacement of the sample. It is shown in Fig. 2(b) which represents a section of the insert in the $x-z$ plane. With the aid of a screw G, which is in contact with the ball-shaped part F, a pivoting motion of the arm D is induced around the hinge H_2. This pivoting motion is translated into a movement of lens L over a small segment of a circle almost parallel to the x direction. The maximum displacement of the lens along x is 1.0 mm with a resolution of 1 μm. The rotation of the screw G is controlled by a wormwheel W_2 which is also connected to a knob at the top of the cryostat. A leaf spring LS provides the necessary mechanical tension to achieve a reproducible backlash-free movement of the lens. This adjustment is decoupled from the movement of the sample along the y direction because the pins connected with the frame holding the LiF substrate are allowed to slide through the holes A.

The procedure for achieving the optimum focusing of the laser beam on the sample is as follows. First the tube, which contains the lens L, is screwed into its fitting to obtain the optimum focus at room temperature. Then this position is corrected to compensate for the expected increase of the focal length upon the immersion in superfluid helium resulting from the index of refraction of this fluid. The range of about 1 mm of the fine adjustment, induced by the tilting of the arm D by the screw G, is sufficient to tune the lens into the

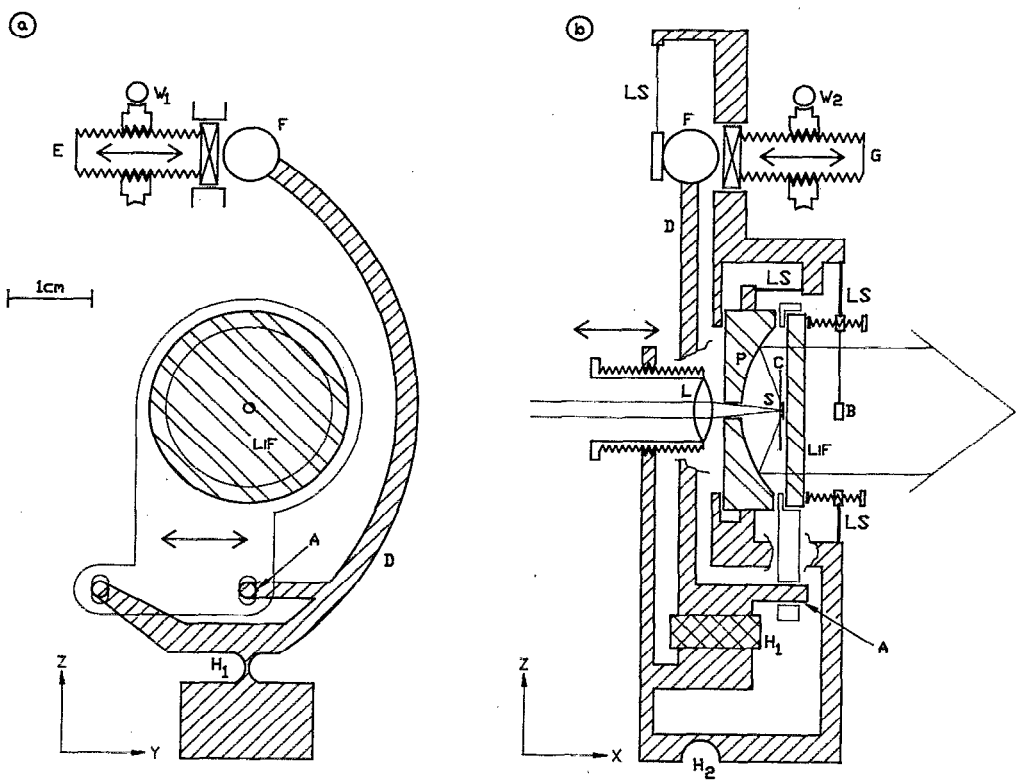

FIG. 2. (a) A section of the insert in the $y-z$ plane showing the principle of the horizontal adjustment of the sample. For further explanation see the text. (b) A section of the insert in the $x-z$ plane showing the principle of the adjustment of the focusing lens L. For further explanation see the text.

proper position. This final optimization is done in two steps. First the sample holder is adjusted such that the excitation light hits the aluminum dot close to the sample [see Fig. 1(b)]. The backreflected beam is inspected on a screen while fine tuning the position of the lens. If the light is properly focused on the aluminum dot a collimated backreflected beam is observed (autocollimation). The focal position obtained in this way is close to the optimal position and only a slight readjustment is needed. In the second step the sample is moved into the excitation beam and the final alignment is achieved by optimizing the statistical fine structure.[4]

The sample can be exposed to microwave radiation in a frequency range of 1–10 GHz with the help of a small loop (I) mounted on the backside of the LiF plate [see Fig. 1(a)]. This loop is connected to a coaxial cable (RG 316/U NM) which in turn is connected to the microwave oscillator.

To perform optically detected magnetic resonance experiments in the presence of a magnetic field the insert is positioned into the central bore of a homebuilt, superconducting magnet [M in Fig. 1(a)]. This magnet is mounted in a Helmholtz configuration with the magnetic field parallel to the z axis. The central bore of this magnet is 40 mm and the distance between the coils is 52 mm. A magnetic field of 1.3 T can be produced at the position of the sample with a current of 70 A. In view of the small excitation volume the inhomogeneity of the magnet presents no problem. The calibration of the magnetic field was performed with the aid of an electron paramagnetic resonance experiment using a sample of DPPH (diphenylpicrylhydrazyl radical) and yielded the value 18.8 mT/A.

III. PERFORMANCE

An attractive feature of the insert is the possibility to scan the laser beam over the sample. As an illustration of this aspect we present results obtained on a crystal of p-terphenyl doped with pentacene. The $S_1 \leftarrow S_0$ fluorescence–excitation spectrum shows four inhomogeneously broadened zero-phonon lines O_1, O_2, O_3, and O_4 which are related to the four inequivalent sites of the p-terphenyl host crystal. In Fig. 3 the O_1 spectral region is shown as a function of the position of the laser spot on the sample along the y axis. The sample position is indicated by the dial reading of the knob which controls the screw E and is given in arbitrary units. The change in position between reading Nos. 175 and 520 is 1.3 mm. The advantage of moving the sample while keeping the lens L and the parabolic mirror P fixed is that the light collection optics needs no readjustment for the different sample positions. It is obvious from Fig. 3 that the shape of the spectral line depends strongly on the position of the laser focus, an effect which is caused by variations in local strain across the sample. Upon reading No. 520 a narrow inhomogeneous line with a width of 700 MHz (full width at half-maximum) is observed, which exhibits a satellite structure caused by the presence of pentacene molecules containing ^{13}C.[8,9] As evidenced by the spectra the observation of these satellites requires a crystal region with very little strain. The results of Fig. 3 show that the present arrangement is ideally suited to find such regions.

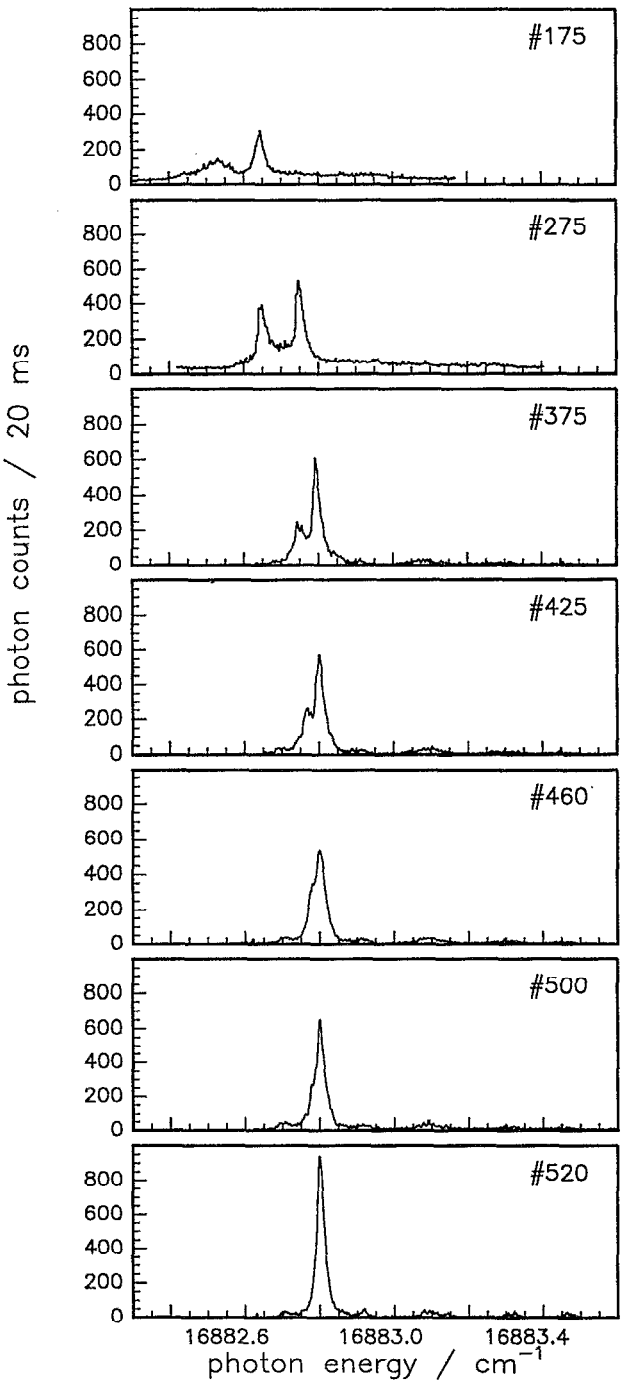

FIG. 3. Fluorescence-excitation spectra of pentacene in p-terphenyl in the region of the $S_1 \leftarrow S_0$ transition of the O_1 site for different positions of the sample in the exciting light beam. The sample positions are given by the dial reading of the knob controlling the movement of the sample. Starting from the top box the dial is changed gradually from Nos. 175 to 520 corresponding to a movement of 1.3 mm of the sample. It is seen that the narrowest line occurs for dial reading No. 520. The laser power incident to the cryostat was 1 nW which corresponds to 5 mW/cm^2 when in focus.

To illustrate the effect of the positioning of the focusing lens L on the excitation spectra we present in Fig. 4 several recordings obtained by scanning the laser over a range of 500 MHz in the red wing of the inhomogeneously broadened $S_1 \leftarrow S_0$ transition. The upper trace shows a spectrum taken

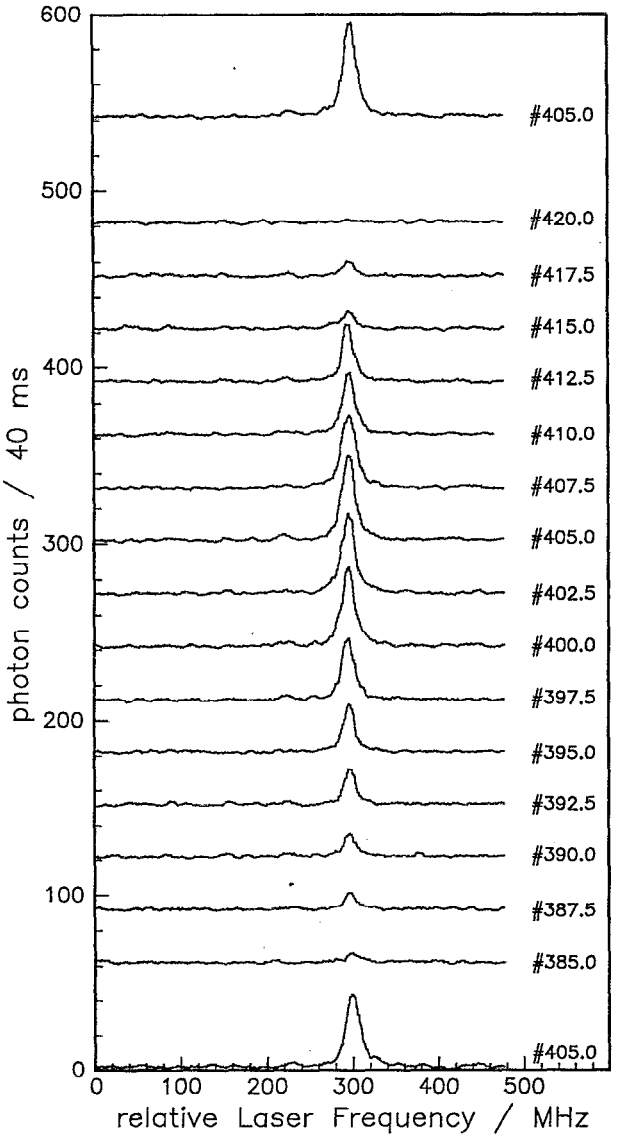

FIG. 4. Fluorescence-excitation spectra of a single molecule of pentacene in p-terphenyl obtained by scanning a single-mode laser over a range of 500 MHz in the red wing of the inhomogeneously broadened $S_1 \leftarrow S_0$ transition for the O_1 site. The laser frequency is given in relative units. The spectra have been obtained for different settings of the dial controlling the position of the focusing lens L. The laser power incident to the cryostat was 5 nW corresponding to 25 mW/cm^2 when in focus. The vertical scale is valid for the lowest trace while the other traces were offset for clarity. For further explanation see the text.

with the lens L at position No. 405. In the center we see the fluorescence excitation line of a single molecule. While the distance between the lens and sample is changed over a range of 50 μm between setting Nos. 420 and 385, the initial spectrum is reproduced again at setting No. 405. After completing the whole sequence, the original spectrum was found back at setting No. 405 (the lowest trace). The fact that the spectrum is so well reproduced shows that the backlash in the lens positioning is negligible.

In Fig. 5 the effect of the magnetic field on the optically detected magnetic-resonance signal of a single pentacene-

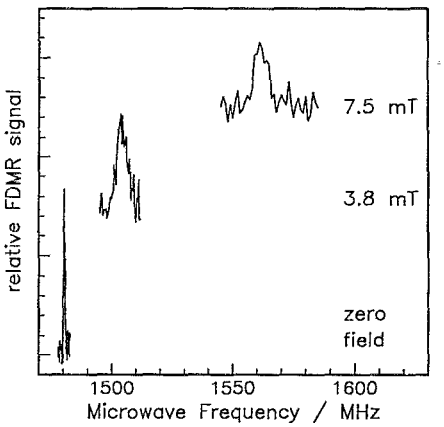

FIG. 5. Fluorescence-detected magnetic-resonance spectra of a single pentacene-d_{14} molecule in p-terphenyl-d_{14} in zero-magnetic field, in a field of 3.8 mT and in a field of 7.5 mT.

d_{14} molecule in a p-terphenyl-d_{14} host is shown. In zero field the signal corresponds to the T_x–T_z transition at 1480.4 MHz with a linewidth of 670 kHz. Upon the application of a small magnetic field the transition shifts to higher frequency and moreover exhibits a considerable line broadening. The broadening results from the hyperfine interaction with the deuterium spins which is forbidden in first order in zero field. A detailed analysis and discussion of these data will be presented elsewhere.

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