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Linear dichroism in the absorption and triplet-state excitation spectra of F_2 centers in KCl

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The absorption and triplet-state excitation spectra of aligned and unaligned F_2 centers in KCl at liquid-nitrogen temperature have been measured by means of the polarization modulation of visible light. A new technique involving the selective deexcitation of the triplet state of F_2 centers of specific orientations has been developed. Evidence for both an indirect and a direct triplet-state excitation mechanism is presented. The results have permitted the identification of the symmetry representations of the excited states of a number of transitions. In particular, the results indicate that the M_4 band at 634 nm terminates on a $^3\Pi_u$ state which includes a spin-orbit admixture of $^1\Sigma_u^+$. The spin-orbit coupling parameter has been evaluated at 0.062 ± 0.003 eV. The triplet-triplet transition at 505 nm is shown to include both polarizations perpendicular to the defect axis and thus terminates on a $^3\Pi_g$ level. An energy-level diagram for the F_2 center is presented.

I. INTRODUCTION

Early work on the dichroic properties of F_2 centers (called M centers in the older terminology) in KCl by Okamoto[1] and Haarer and Pick[2] uncovered a number of electronic transitions in the visible and near-infrared. Most of these experiments involved measuring the absorption and excitation spectra of partially aligned F_2 centers using light polarized in various directions with respect to the defect axis.

Since these experiments were done, much more sensitive techniques involving the polarization modulation of light have become available. These techniques present two important advantages over the older methods: First, they are far more sensitive; second, they are sensitive only to centers of a particular symmetry. For this latter reason, one may avoid effects arising from the very strong absorption of the F centers, absorption which tended to mask transitions lying under the F band.

The present experiments extend this earlier work on aligned F_2 centers by using the polarization-modulation technique. In addition, I will describe the results of a new technique involving the deexcitation of the metastable triplet state of F_2 centers having certain specific orientations. The results of these experiments yield the energy and polarization of a number of transitions. Quantitative measurements of the relative strengths of the M_1 and M_4 bands at 800 and 634 nm, respectively, were made.

The results provide information on the symmetry of the wave functions of various energy levels and on the nature of the singlet-triplet conversion. This kind of information will be useful for the research presently being undertaken on triplet-singlet reconversion and, in particular, on the lifetime of the lowest triplet state.

The present research will be described in the following five sections. In Sec. II is given a brief résumé of F and F-aggregate centers and their production and properties. The experimental apparatus for linear dichroism spectra is described in Sec. III. Section IV presents the experimental results of the measurements of the absorption and excitation spectra of aligned F_2 centers, and Sec. V the results of the deexcitation of the triplet state of nonaligned centers. Finally, a simple qualitative group-theoretical treatment of the results is given in Sec. VI.

II. BACKGROUND

An F center consists of an electron trapped at a negative-ion vacancy.[3] This type of defect gives rise to a number of absorption bands,[4] the most important of which are the F band, at 539 nm at liquid-nitrogen temperature, and the K band at 460 nm.

A crystal containing F centers invariably contains aggregates of near-neighbor F centers.[5] The simplest of these is the F_2 center, consisting of two F-center electrons occupying nearest-neighbor Cl^- sites, which are along the six equivalent $\langle 110\rangle$ directions. This center gives rise to a number of absorption bands, the strongest being the M_1 band, which lies at about 800 nm. An F_3 center (or R center in the older terminology) consists of three F-center electrons occupying the three nearest-neighbor Cl^- sites forming an equilateral triangle in the four equivalent $\{111\}$ planes. This center gives rise to absorption bands at 658 and 730 nm, the R_1 and R_2 bands, respectively.

Irradiation at room temperature of a crystal containing F centers by light in the F band causes agglomeration of the F centers[6]; the result is an increase in the absorption of the M_1, R_1, and R_2 bands with a concomitant decrease in F-band absorption.

Following the analysis of Aegerter and Lüty[7] for the F_2^+ center, we may define an internal coordinate system for the F_2 center. We define the z axis of the coordinate system to be along the axis of the defect which, for convenience, we will take to be in the [011] direction with respect to the crystal axes. We then take the y axis along [100] and x along [0$\bar{1}$1].

Okamoto[1] measured the difference in optical density of a KCl crystal containing aligned F_2 centers for light of various polarizations. His results showed that the M_1 band is a z-polarized transition, as is the M_4 band, at 634 nm. The M_2 and M_3 bands at 546 and 490 nm are x transitions, while the M_2' and M_3' bands at 538 and 480 nm are y.

The ground state of the F_2 center is a spin singlet level, and Okamoto's results apply to singlet-singlet transitions. The work of Haarer and Pick[2] concerned principally transitions between the triplet-state levels. EPR experiments by Seidel[8] established the existence of a nearly metastable triplet-state level having a lifetime of from about 50 to 100 sec depending upon the degree of room-temperature agglomeration of the crystal.[9] The triplet ground state may be populated by irradiating the crystal in the F band. (This optical pumping is usually done at liquid nitrogen temperature or below to avoid additional agglomeration of the centers.) In this way, Schneider and Caspari[10] and Haarer and Pick[2] identified transitions at 505, 600, and 685 nm as triplet-triplet transitions. In addition, the latter group optically pumped a KCl crystal containing partially aligned centers with light polarized parallel and perpendicular to the defect axis. They found that the two excitation spectra were somewhat different.

A number of proposals have been made to explain the mechanism by which the lowest triplet level is populated as a result of F-band irradiation.[11-15] Most of these proposals involve the displacement of an electron between F and F_2 centers.

III. EXPERIMENTAL PROCEDURES

Single crystals of KCl were purchased from the Harshaw Chemical Co. and γ irradiated at dry-ice temperature with 5×10^6 R from a ^{60}Co source. The sample was then cleaved to 5.4×5.4 mm and polished. In order to agglomerate the F centers, the sample was irradiated at room temperature for 8 min on each face with light from a 250-W tungsten source passing through at 560-nm interference filter. Then the sample was placed in position on the cold finger of a cryostat and the temperature reduced to approximately 80 K, the temperature at which all subsequent experiments described here were carried out. The F_2 centers were aligned along the [011] direction by a 10-min irradiation on each face with the 496.5-nm 600-mW transition of a 5-W argon laser. The absorptions in the M_1 band at 800 nm for light polarized along [011] and [0$\bar{1}$1] were measured on a Cary 14 spectrophotometer employing Polaroid HR infrared polarizing filters in the monitor and reference beams. The optical densities were found to be 1.49 and 0.13, respectively. If we define the degree of alignment as the concentration of F_2 centers along [011] divided by the total concentration, including all six equivalent orientations, these figures represent an alignment of approximately 80%. (Details of the alignment procedure and relevant calculations are given fully in the article by Aegerter and Lüty.[16]) Using Smakula's equation[17] and the value 1.49 for the optical density, the concentration of F_2 centers aligned along [011] is found to be 1.3×10^{16} cm^{-3}. The optical density of the F band, at 539 nm, was 2.23, a figure corresponding to an F-center concentration of 1.8×10^{16} cm^{-3}.

The linear dichroism of a crystal is defined as follows: If unpolarized light is incident upon the crystal, and an intensity $I_{\parallel}$ of light emerges with polarization parallel to a given axis, and $I_{\perp}$ is the intensity of the perpendicular polarization, then the linear dichroism of the crystal is

$$p=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}} . \tag{1}$$

If $\alpha_{\parallel}$ is the absorption coefficient for the light parallel to the axis, we have

$$I_{\parallel}=I_{\parallel 0}\,e^{-\alpha d} , \tag{2}$$

with a similar expression for $I_{\perp}$. Since we assume that the incident light is unpolarized, we will have $I_{\parallel 0}=I_{\perp 0}$ and p becomes

$$p=\frac{e^{-\alpha_{\parallel}d}-e^{-\alpha_{\perp}d}}{e^{-\alpha_{\parallel}d}+e^{-\alpha_{\perp}d}} . \tag{3}$$

It is convenient to make the following definitions:

$$a\equiv\tfrac{1}{2}(\alpha_{\perp}d+\alpha_{\parallel}d) , \tag{4}$$

$$\Delta a_{\perp-\parallel}\equiv\tfrac{1}{2}(\alpha_{\perp}d-\alpha_{\parallel}d) , \tag{5}$$

so that

$$\alpha_{\parallel}d=a-\Delta a_{\perp-\parallel} \tag{6}$$

and

$$\alpha_{\perp}d=a+\Delta a_{\perp-\parallel} . \tag{7}$$

Substituting into (3) gives simply

$$p=\tanh\Delta a_{\perp-\parallel} . \tag{8}$$

It should be noted that for most of the experiments described here the dichroism signal is positive when the perpendicular absorption is greater.

Figure 1 shows the apparatus used in measuring this quantity together with the laboratory coordinate system *XYZ*, which will be employed in all subsequent discussion of the geometry. Light from a 30-W tungsten lamp travels in the [100] direction and is focused upon the entrance slit of a 25-cm Jarrel Ash monochromator having a spectral bandwidth of 3 nm. The emerging monochromatic light then passes a Nicol prism which transmits only the vertically polarized [001] component. Following this prism is a photoelastic modulator of the type developed by Jasperson and Schnatterly[18] and Kemp.[19] This device modulates the polarization of the light at 50 kHz between left-hand and right-hand circular. The polarization-modulated light is incident upon a fixed quarter-wave plate, which consists simply of a piece of flat glass mounted in a small mechanical press. By increasing the pressure on the glass one increases the refractive index for light polarized parallel to the direction of the force. Thus one may easily achieve quarter-wave retardation for any desired wavelength.

Figure 2 shows two orientations of the quarter-wave plate. With the retardation axis vertical, as shown at the top of the figure, left-hand circularly polarized light emerges linearly polarized along the [011] direction; the right-hand polarization emerges linearly polarized along [0$\bar{1}$1]. Thus, the polarization of the emerging light is switched between the two diagonal directions, and I shall refer to this configuration as "dd switching." If the fixed quarter-wave plate is mounted with its retardation axis at 45° to the vertical (Fig. 2, bottom), the emergent light is switched between the horizontal, [010], and vertical, [001], directions; this I shall call "hv switching."

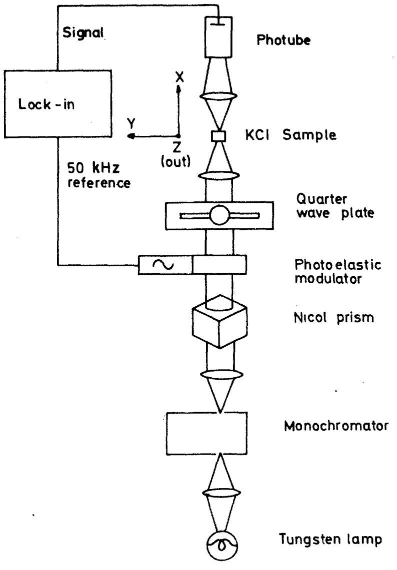

FIG. 1. Apparatus used in measuring the linear-dichroism spectra. The optical-bench coordinate system is also shown.

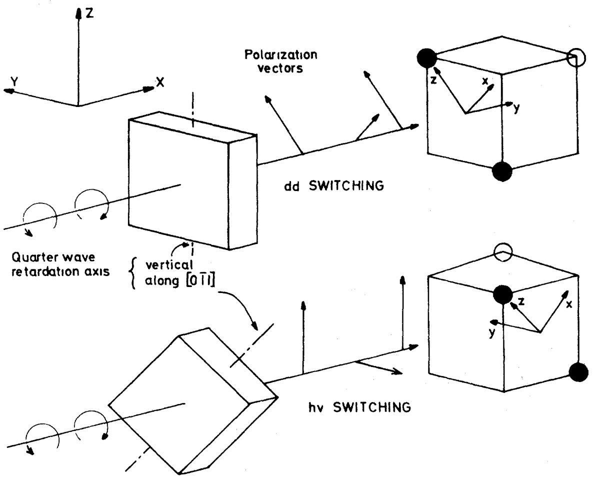

FIG. 2. Quarter-wave plate and crystal **orientations** for dd and hv switching. Modulated circularly polarized light is shown incident from the left. At the right are shown unit cells, each containing an F_2 center represented by the solid circles. The open circle represents the position of a third *F* center electron giving rise to an F_3 center. The three independent transition moments of the F_2 center lie along the *x*, *y*, and *z* axes shown in each unit cell.

The linearly polarization-modulated light is then focused upon the sample and detected with an EMI 9558QB photomultiplier tube. A difference in the absorption coefficients for the two mutually perpendicular polarizations will result in an amplitude modulation at 50 kHz of the phototube output current. This signal is then amplified with a lock-in detector. A feedback circuit in the phototube power supply adjusts the phototube high voltage so that the output current, which is proportional to the denominator in (1), is held constant. In this way the lock-in signal is made directly proportional to the linear dichroism and is unaffected by an absorption, such as that due to *F* centers, having no polarization dependence.

At the top right-hand side of Fig. 2 is shown a unit cell containing an F_2 center, represented by the solid circles, in the [011] direction. The axes of the three independent transition moments are shown and labeled following the notation of Aegerter and Lüty.[7] If the absorption coefficients for light polarized along *x*, *y*, and *z* are α_x, α_y, and α_z, we have from (5)

$$\Delta a_{x-z} = \tfrac{1}{2}(\alpha_x d - \alpha_z d) \ . \qquad (9)$$

The hv configuration, as shown at the bottom of Fig. 2, is slightly more complicated. In this configuration the crystal is rotated by 90° so that the F_2 centers lie along the $[\bar{1}01]$ direction. The absorption coefficient for light polarized vertically becomes

$$\alpha_v = \tfrac{1}{2}\,\alpha_z + \tfrac{1}{2}\,\alpha_x \;. \tag{10}$$

The expression for the differential absorption, (5), becomes

$$\Delta\alpha_{h-v} = \tfrac{1}{2}\,(\alpha_y d - \tfrac{1}{2}\,\alpha_z d - \tfrac{1}{2}\,\alpha_x d) \;. \tag{11}$$

The open circle of the unit cells shown in Fig. 2 represents the position of a third F-center electron which, in combination with the other two, gives rise to an F_3 center. For the dd configuration we see that the x and z directions indicated are not equivalent for the F_3 center, and we may expect to see dichroic effects arising from this center. This, however, is not the case for the hv configuration, wherein the h and v directions *are* equivalent. Thus, the hv configuration has the very important advantage of being sensitive only to the F_2 center and its charged equivalents, F_2^+ and F_2^-.

IV. SPECTRA OF ALIGNED F_2 CENTERS

A. Singlet absorption spectra

Curves a and b of Fig. 3 show the absorption spectra of the aligned F_2 centers for the dd and hv configurations, respectively. All of the transitions identified by Okamoto are readily identifiable, although in the case of the M_2 and M_2' band the wavelengths do not quite agree.

On curve a the M_2 band is shown peaking at about 553 nm. The maximum corresponds to a dichroism of about 40%, and the transition is x polarized. (Okamoto gave 546 nm for its wavelength.) The M_3 band, the bump to the high-energy side of M_2, is not resolved from M_2, but it is clearly x polarized, and the wavelength given by Okamoto, 490 nm, is not inconsistent with this curve. On this curve we also see the two F_3-center transitions, the R_1 and R_2 bands at 658 and 730 nm, respectively. The R_1 band overlaps the M_4 band at 634 nm. Finally, the z-polarized M_1 band appears at 800 nm. It should be mentioned that for these curves the quarter-wave plate and the amplitude of the photoelastic modulator were adjusted for maximum sensitivity at 570 nm. As a result, at 800 nm the sensitivity has decreased by a factor of 2 or so, owing to the fact that quarter-wave retardation is no longer achieved. Hence, the M_1 band is significantly stronger, relative to the M_2 band, than it appears in Fig. 3.

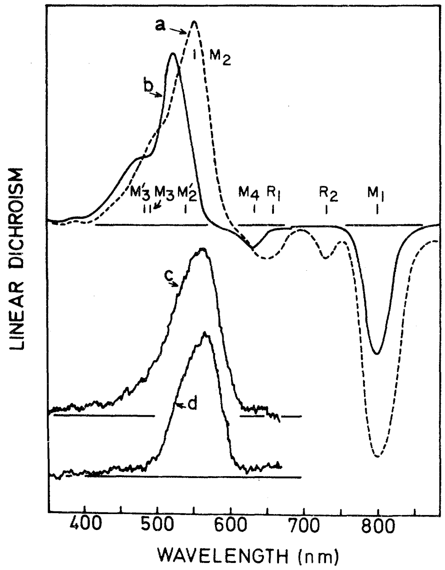

FIG. 3. Absorption and triplet-state excitation spectra of the F_2 center. Curve a: linear dichroism for the dd configuration; curve b: linear dichroism for the hv configuration. Prominent transitions are labeled. On curve b the gain was reduced by a factor of 4 for wavelengths longer than 670 nm. Positive values correspond to a greater absorption of the component of polarization perpendicular to the defect axis. Curves c and d: excitation spectra of the lowest triplet state taken by monitoring the 685-nm triplet band in the hv configuration while sweeping the pump light vertically polarized (curve c) and horizontally polarized (curve d). For the four curves the gain was adjusted for maximum sensitivity so that the vertical scale is different for each curve.

Curve b shows the spectrum for the hv configuration. The M_2' transition is y polarized and is shown peaking at 523 nm, but for this configuration the y and the x transitions are not completely resolved. Hence, the 538-nm wavelength that Okamoto found for this transition is probably about right. The peak of the M_2' transition corresponds to a linear dichroism of approximately 18%. At 670 nm the lock-in gain was reduced by a factor of 4, on this curve, so that the M_1 band would remain on scale. The M_3' band is clearly visible, also as a y transition, and is almost resolved on the high-energy side of the M_2' band. The M_3' wavelength is 480 nm. For the hv configuration the M_4 band is no longer obscured by the R_1 band and is seen clearly as the z-polarized peak at 634 nm.

B. Triplet-state excitation spectra

In order to learn more about the mechanism by which the lowest triplet-state level of the F_2 center is populated, excitation spectra of this level were measured. The principal triplet-triplet transition occurs at 685 nm, and this transition is known to be z polarized.[2] Thus the differential absorption, (11), becomes

$$\Delta a_{\text{h-v}} = -\tfrac{1}{4}\,\alpha_t d\ , \tag{12}$$

where α_t is the absorption coefficient for the triplet band. The linear dichroism, (8), becomes

$$p = -\tanh(\tfrac{1}{4}\,\alpha_t d)\ . \tag{13}$$

For these experiments the dichroism induced in the triplet band is quite small, at most 1% or so, so that it is a very good approximation to expand the hyperbolic tangent and disregard the higher-order terms. Hence

$$p = -\tfrac{1}{4}\,\alpha_t d\ , \tag{14}$$

and since α_t is proportional to the triplet-state population, we see that the linear dichroism is directly proportional to this population to a high degree of accuracy.

Farge[9] has measured the dichroism induced in the triplet band of unaligned F_2 centers for optical pumping with polarized light in the spectral region of the M_3 and M_3' bands. He found a strong correlation between the dichroism induced and the lifetime of the triplet state. He concluded that two types of F_2 centers are present. One of these is perturbed by an F center in close proximity and has a lifetime at 4 K of 56 sec; the other is isolated and has a longer 96-sec lifetime. Furthermore, the triplet state of the perturbed F_2 center may be excited indirectly by first exciting the nearby F center, and thus it is insensitive to the polarization of the pump light. The isolated, or "pure," F_2 may be excited directly. The method of preparation and the observed triplet-state lifetime (about 50 sec at 80 K) of the sample used in the present experiments indicate that the F_2 centers are rather highly perturbed and thus should be relatively insensitive to the polarization of the pump light.

In the experiments described here the apparatus for measuring the excitation spectra is quite similar to that for the absorption measurements. The triplet band was monitored by replacing the Jarrel Ash monochromator by a Jobin-Yvon prism monochromator. The optics were adjusted for maximum sensitivity at 685 nm. The Jarrel Ash was then used to sweep the wavelength region from 350 to 650 nm sufficiently slowly to allow the triplet-state population to reach equilibrium. A red interference filter was placed in front of the phototube to prevent its flooding by the pump light. The pump light was focused onto the sample roughly along the $[\bar{1}00]$ direction, that is, opposite to that of the 685-nm monitor light but slightly abaxial, so that the pump-light optics would not obscure the monitor light.

Two excitation spectra were measured. In the first, shown as curve c of Fig. 3, the pump light was vertically polarized, that is, polarized in the plane of the F_2-center x and z transitions. In the second spectrum, curve d, the light was horizontally polarized, that is, along y. In Fig. 3 these curves have been inverted in sign to facilitate comparison with the absorption spectra. The maximum dichroism induced by pumping at 567 nm was less than 0.1%. (The intensity of the pump light, it should be emphasized, was extremely weak.)

If the lowest triplet level is populated by a process involving a direct excitation of the F_2 center into one of its higher excited states, one would expect strong correlations between curves a and c and between curves b and d. As is seen, no such correlation is evident, and the triplet-state population seems to be almost, but not completely, independent of the polarization of the exciting light.

C. Polarization dependence of triplet-state excitation

In order to investigate more carefully and accurately the polarization dependence of the excitation spectra, a differential measurement was made. The Jarrel Ash monochromator and light source were replaced by a more powerful Bausch and Lomb combination tungsten lamp and 10-cm-grating monochromator having a spectral bandwidth of 16 nm. Because the light from this monochromator is partially polarized, a Polaroid filter with the transmission axis at 45° to the vertical was placed in the beam. This was followed by a second Polaroid whose axis could be rapidly changed from a horizontal to a vertical direction. This combination assured that the intensities of the vertically and horizontally polarized pump light were equal. At each exciting wavelength the sample was pumped with horizontally polarized light and the triplet-band dichroism p_{h} was recorded. Then the second polarizer was rotated to allow the transmission of vertically polarized pump light and the dichroism p_{v} was recorded. Then the pump light was turned off and the triplet decay monitored in order to establish an accurate base line; this was necessary due to the presence of a previously unreported effect to be described later. Having measured p_{h} and p_{v}, the *pumping efficiency ratio* was defined as

$$\text{efficiency ratio} = p_{\text{v}}/p_{\text{h}}\ . \tag{15}$$

The values so obtained are shown in Fig. 4.

If the triplet-state population is completely independent of the polarization of the pump light, as for an indirect excitation mechanism, we expect an efficiency ratio of 1. If, on the other hand, triplet-state population results from pumping a

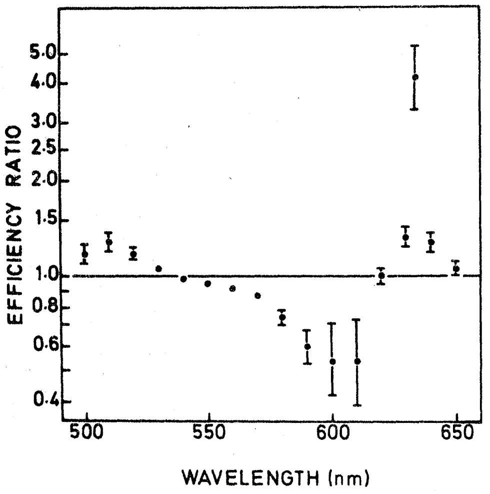

FIG. 4. Efficiency ratio of the two polarizations of pump light. The points show the value of the dichroism of the triplet band at 685 nm, when pumping aligned F_2 centers in the hv configuration with vertically polarized pump light, divided by this value when pumping with horizontally polarized light.

strongly polarized F_2-center transition, this ratio would deviate significantly from 1. If, for example, the transition is strongly z polarized, the ratio would rise to a value as high as 10 or so. (It would not be infinite, due to the fact that the pump-light direction is not exactly along $[\bar{1}00]$, so that the horizontal polarization includes a small component in the F_2-center z direction.) If both excitation mechanisms are present, we would expect intermediate values. As is seen in Fig. 4, the efficiency ratio rises sharply to a value of approximately 4 when pumping in the M_4 band, indicative of a direct excitation of the F_2 center into its triplet state for this wavelength. However, between 500 and 620 nm the efficiency ratio varies between 1.3, at 510 nm, and 0.5, at 600 nm. At the strong y transition at 523 nm, curve b of Fig. 3, one would expect more efficient h pumping and therefore an efficiency ratio of less than 1.0. Similarly, at the long-wavelength side of the F band, where the x transition is strong, one would expect efficiency ratios greater than 1. In both regions the opposite is the case.

Lifetime measurements of the lowest triplet-state level by Ortega[20] indicated that irradiation in the triplet band at 685 nm caused a rapid reconversion to the singlet state. The same process seems to be occurring at the triplet bands of 505 and 600 nm. The 600-nm triplet transition is z polarized,[2] so that when pumping with vertically polarized light, the same light responsible for populating the lowest triplet level also partially depopulates this level. Such is not the case for horizontally polarized pump light. This selective depopulation, then, accounts for the lesser pump efficiency of v light at 600 nm. As will be shown below, the 505-nm transition includes a strong y-polarized component, so that v pumping, which does not induce this transition as strongly as h pumping, is more effective, leading to an efficiency ratio greater than 1 in this region. Allowing for this effect, it is seen that the pumping efficiency in the 500–620-nm region is relatively independent of polarization.

Several workers[12, 14, 15] have found evidence for an electron-transfer mechanism to account for singlet-triplet conversion of F_2 centers. In this mechanism an F center absorbs a photon and loses its electron, leaving a negative-ion vacancy called an α center. The electron is trapped by an F_2 center forming an F_2^- center. This center in turn decays, giving an electron back to the α center, and may leave the F_2 center in its triplet state. In such a process the triplet-state populations would be independent of the polarization of the pump light. Thus, the data of Fig. 4 are consistent with such a mechanism for the wavelength range up to the M_4 band. For this wavelength an alternate mechanism will be described in Sec. VI.

The uncertainties of the points shown in Fig. 4 originated from two sources. First, the points had to be taken rather quickly, within a minute or two, in order to avoid too great a disalignment of the centers during optical pumping. For this reason the base line was, in some cases, not too well established. Second, a very great shift in the dichroism base line for equilibrium with no pumping occurred as a result of having irradiated the sample in the region from about 570 to 650 nm.

The effect is illustrated more clearly in Fig. 5. First, the sample is irradiated at 634 nm with vertically polarized light from the Bausch and Lomb monochromator for 20 min. Then the light is turned off and the sample allowed to come to equilibrium in the dark for 10 min or so, so that the triplet-state population is essentially zero. A measurement of the linear dichroism as a function of wavelength between 660 and 760 nm yields the dashed curve of Fig. 5. Now the sample is reirradiated at 634 nm for 20 min, but with horizontally polarized light, the light turned off, and the sample allowed to come to equilibrium as before. Another measurement of the linear dichroism yields the solid curve. The maximum change in the dichroism occurs at about 738 nm, although the change may be somewhat obscured by the M_1 band seen at the right of the figure. This maximum change corresponds to a dichroism of about 0.5%. At liquid-nitrogen temperature these two curves are stable, and the effect is completely

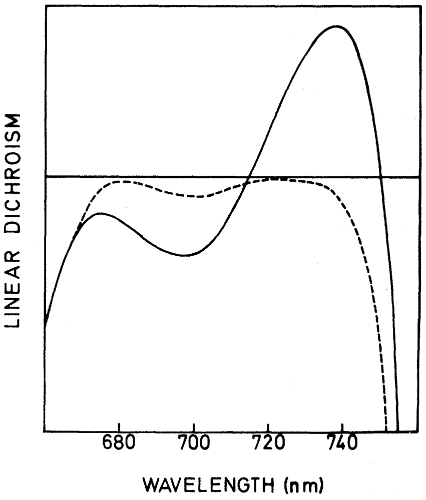

FIG. 5. Unexplained change in the dichroism base line. Dashed curve: linear dichroism in the hv configuration of the crystal containing aligned F_2 centers after 20 min of irradiation at 634 nm with vertically polarized light followed by 10 min in the dark. Solid curve: same as above but using horizontally polarized pump light instead. The maximum shift in the base line is about 0.5%. F_2^- centers may be responsible.

reversible. Although the effect is greatest for irradiation in the region of the M_4 band, this is likely to be a coincidence, since the effect is observed for pumping at wavelengths shorter than the M_4 band as well. Farge[21] observed a dichroic band in lithium fluoride which lies between the R bands, which is stable at 77 K, and which disappears upon irradiation in the band. This band proved to originate from F_2^- centers. Since the energy and general characteristics are similar to those of the 738-nm band in KCl, it is certainly not unreasonable to suppose, tentatively, that this band also originates from F_2^- centers. Further investigations of the effect have not as yet been carried out.

V. TRIPLET DEEXCITATION SPECTRUM OF UNALIGNED F_2 CENTERS

It is possible to induce a rather large linear dichroism in the triplet band at 685 nm in a KCl crystal containing randomly oriented F_2 centers by optically pumping the sample with polarized light.[22] In such an experiment a γ-irradiated sample having an F-center concentration of about 5×10^{16} cm^{-3} and no room-temperature agglomeration was used. Such a sample assured a high degree of homogeneity of concentration and random orientation of F_2 centers. As before, the triplet-band dichroism was monitored using the Jobin-Yvon monochromator and the pump source was the Bausch and Lomb monochromator followed by a Polaroid filter with its transmission axis horizontal. The hv configuration was used, again to avoid detecting F_3-center absorptions. The geometry is shown in Fig. 6; the six orientations of the F_2 center are numbered.

The results of the experiment are shown in Fig. 7 and are easily interpretable in view of the results on aligned centers described in Sec. IV. In Fig. 7 positive values of dichroism correspond to a greater absorption of the vertically polarized component of the 685-nm triplet-band light.

When pumped at 634 nm, where the F_2 triplet is excited directly, centers 5 and 6 are excited, since the M_4 band is z polarized. Because the 685-nm transition is also z polarized, the horizontal component of the monitor light is slightly absorbed, giving the negative dichroism shown. The unusual shape of the transition is due to leakage of backscattered pump light through the red filter in front of the phototube; this leakage greatly reduced the sensitivity for wavelengths above 625 nm.

The triplet-state excitation spectra of curves c and d of Fig. 3 indicate that the maximum triplet-state populations occur for irradiation at 567 nm. This excitation is insensitive to the polarization of the pump light, and all six centers are populated uniformly. However, the spectral pass band of the Bausch and Lomb monochromator overlaps the z-polarized triplet band at 600 nm. Thus the pump light partially depopulates the triplet state of centers 5 and 6. This leads to a greater absorption of the vertical component of the monitor light. The maximum value of the dichroism[23] in Fig. 7 was about 2.8% and occurred at 570 nm. A similar thing happens at 505 nm, except that triplets of centers 3 and 4 are depopulated because the h-polarized component of the absorption is greater

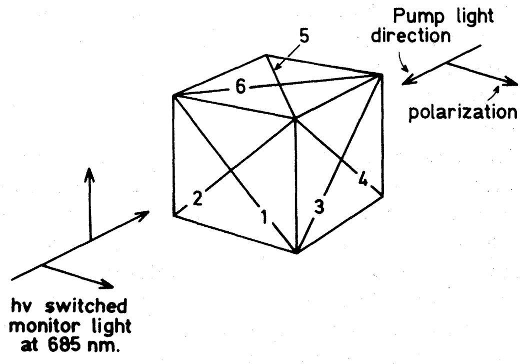

FIG. 6. Geometry for polarized optical pumping of unaligned F_2 centers. The six possible orientations of the centers are numbered.

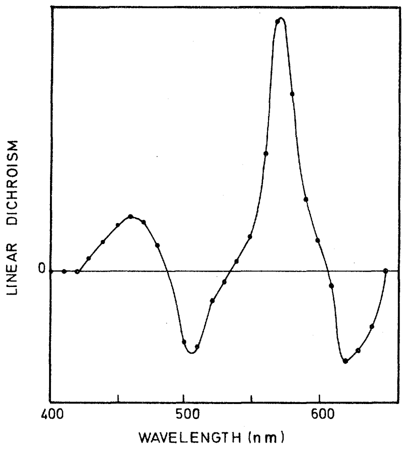

FIG. 7. Dichroism induced in the 685-nm triplet band as a result of horizontally polarized optical pumping at the wavelength shown. Positive values correspond to a greater absorption of the vertical component of the monitor light.

than the v component; that is, $\alpha_y > \frac{1}{2}\alpha_x$ in the notation of Eq. (11).

At 460 nm the vertical absorption is again greater, but no triplet transition is known at this wavelength. Perhaps the y-polarized M_3' transition of the F_2 center is being excited, inducing a direct singlet-triplet conversion. The efficiency ratio was not measured here in the previous experiments on aligned F_2 centers for fear of too great a disalignment of the centers, and what is happening is anybody's guess.

Another simple experiment served to add further confirmation to the supposition that triplet-band dichroism may be induced by the selective deexcitation of the triplet states of centers of particular orientations. Since the triplet transition at 685 nm is much stronger than that at 600 nm, deexcitation with polarized light at 685 nm, rather than 600 nm, should greatly increase the observed triplet-band dichroism.

Figure 8 shows the apparatus used. As before, the 685-nm triplet band was monitored using the Jobin-Yvon monochromator with the optics in the hv configuration. The sample was pumped at 570 nm with unpolarized light from the Bausch and Lomb monochromator shown at the left-hand side. At the right-hand side is shown the Jarrell-Ash 25 cm monochromator, having a spectral bandwidth of 6 nm, used to sweep the deexcitation spectrum. A 30-W tungsten lamp was placed at the entrance slit. A Polaroid filter with its axis horizontal was placed in the exit beam.

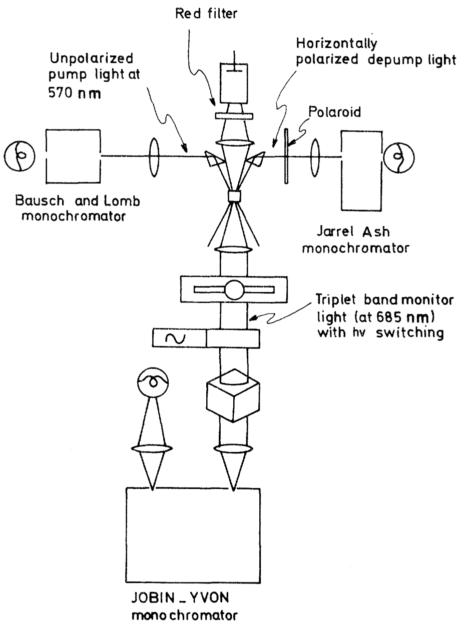

FIG. 8. Apparatus used in measuring the triplet-state deexcitation spectrum. Irradiation with polarized light selectively depopulates the triplet state of F_2 centers of specific orientations.

The resulting deexcitation spectrum is shown in Fig. 9. Positive values correspond to a greater absorption of the horizontally polarized component of the 685-nm monitor beam. As is seen, the three triplet bands, 505, 600, and 685 nm, stand out clearly and unobscured by singlet transitions or by transitions of other centers. As expected, deexcitation at 685 nm was far more effective than at 600 nm. The 505-nm transition is seen

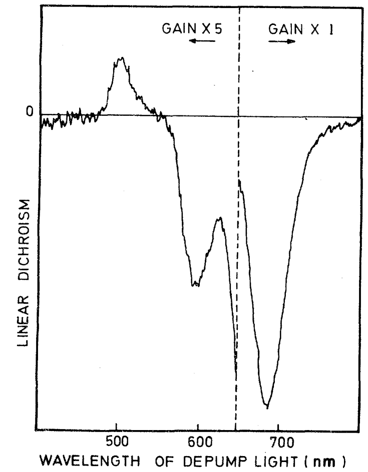

FIG. 9. Triplet-state deexcitation spectrum for hv configuration with horizontally polarized depump light. Positive values correspond to increased transmission of the vertical component of the 685-nm monitor light. The three triplet transitions, at 505, 600, and 685 nm, stand out clearly.

to have a strong y-polarized component; the curve again indicates that $\alpha_y > \frac{1}{2}\alpha_x$. The measurements by Haarer and Pick[2] showed that this transition does in fact have an x component. As mentioned before, they also showed that the 600- and 685-nm transitions are z polarized, in agreement with these results.

VI. ANALYSIS OF RESULTS

The simplest theoretical analysis of the F_2 center was first made by Herman, Wallis, and Wallis.[24] In their model the F_2 center is treated as a neutral hydrogen molecule embedded in a dielectric medium. When the potential felt by the H_2 electrons is reduced by the factor $1/k$, where k is the dielectric constant of the medium, it is found that the Schrödinger equation is unchanged from its free-space form if distances r and energies E scale in the following way:

$$r = r_f/k \tag{16}$$

and

$$E = E_f/k^2 , \tag{17}$$

where r_f and E_f are the distance and the energy for the H_2 molecule in free space. A similar model, that of the H_2^+ molecule in a dielectric, has been applied very successfully to the F_2^+ center in KCl by Aegerter and Lüty.[25]

Unfortunately, I have been unable to obtain accurate calculations of the potential curves for the excited states of molecular hydrogen out to the large interatomic distances necessary. The most useful of such curves appear in an old article by Mulliken,[26] although for those states and at those distances where comparisons are possible, his results do not agree very well with more recent calculations.[27-29] Mulliken's curves yield a value of $k = 2.32 \pm 0.04$ for the dielectric constant when applied to the singlet and triplet transitions at 800 and 685 nm, respectively. This value is very close to that found by Aegerter and Lüty[25] for F_2^+. However, this value was obtained for a free-molecule internuclear separation of 2.75 Å, which corresponds to an anion-anion distance of 6.4 Å, much larger than the actual distance of 4.5 Å in KCl. Nevertheless, important qualitative information concerning the symmetry of the wave functions, the relative positions of the energy levels, and the polarization of the allowed transitions may be obtained from this model.

When considering the H_2 model of the F_2 center, one normally adopts the language of molecular spectroscopy in identifying the energy levels. In this notation the designation of each level also labels the representation according to which the wave function transforms in $D_{\infty h}$, the group of the hydrogen molecule.[30] However, the F_2 center has a site symmetry of D_{2h} which has only one-dimensional representations. Hence the Π states of the hydrogen molecule are split.

Figure 10 shows the energy levels of the F_2 center and their representations, which are most consistent with the results of the present experiments. For clarity the singlet and triplet-state levels have been separated. The levels are labeled first according to the united atom-electron configuration, whenever this is possible; second with the representation of the orbital wave function in $D_{\infty h}$; third with the orbital representation in D_{2h}. The spacing between each of the singlet and each of the triplet levels is to scale. However, the relative spacing of the singlet and triplet levels is not known; efforts to measure, for example, the energy difference between the lowest triplet ($^3\Sigma_u^+$) and singlet ($^1\Sigma_g^+$) levels have so far shown only that the energy lies somewhere between 0.1 and 0.4 eV.[31]

Also shown in Fig. 10 are the transitions investigated in these experiments. These transitions are also summarized in Table I. The origins of the M_1, M_2, M_2', M_3, and M_3' bands and of the 685-nm triplet band have long been suspected.[32, 33] The strength and polarization of the 600-nm triplet band suggest that it is a transition to a higher-lying $^3\Sigma_g^+$ state; the present calculations do not permit the identification of this level with a specific united atom configuration. As mentioned in

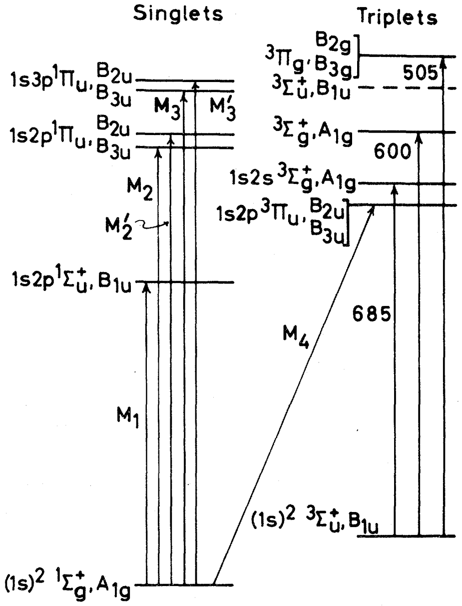

FIG. 10. Energy levels of the F_2 center in KCl. The transitions investigated are indicated by arrows.

TABLE I. Energies and polarizations of the prominent electronic transitions of the F_2 center in KCl.

Band	Wavelength (nm)	Energy (eV)	Predominant polarization
M_1	800	1.55	z
M_2	553	2.24	x
M_2'	538	2.30	y
M_3	490	2.53	x
M_3'	480	2.58	y
M_4	634	1.96	z
triplet	685	1.81	z
triplet	600	2.07	z
triplet	505	2.46	x and y

Sec. V, the 505-nm triplet transition has both x and y components and is therefore likely to terminate on a ${}^3\Pi_g$ level which is not sufficiently split to allow the resolution of the components.

There are three reasons for believing that the M_4 band at 634 nm is a transition allowed by the spin-orbit interaction to the ${}^3\Pi_u$ level. First, as seen in Fig. 3, the M_4 band is strongly z polarized. A singlet-singlet transition with this polarization would require another ${}^1\Sigma_u^+$ level between the M_1 and M_2 levels. The H_2 model allows no such level. Second, the spin-orbit interaction admixes a small amount of the ${}^1\Sigma_u^+$ wave function to each component of ${}^3\Pi_u$. This results in an allowed transition of the observed polarization and approximate energy. Third, the efficiency-ratio data of Fig. 4 show that pumping this transition significantly increases the lowest triplet-state population.

It may be that the ${}^3\Pi_u$ levels are split just as are the ${}^1\Pi_u$, and that we are seeing a transition to only one of the split levels. If so, the other level may lie higher in energy, and the transition to it may be well buried beneath the M_2 bands. If the energy is sufficiently high, the admixture of the ${}^1\Sigma_u^+$ wave function may be so small as to make the transition too weak to detect.

The spin-orbit interaction also allows the admixture of the ${}^1\Pi_u$ wave functions with the ${}^3\Pi_u$, and the ${}^1\Pi_u$ levels are somewhat closer in energy to ${}^3\Pi_u$ than is the ${}^1\Sigma_u^+$ level. A ${}^1\Pi_u$ admixture would yield x- and y-polarized transitions which ought not to lie far from the M_4 band. Nevertheless, such transitions are not seen; careful measurements indicated that the M_4 band is completely without observable structure. This would imply that the ${}^1\Pi_u$-${}^3\Pi_u$ spin-orbit parameter is very small if not exactly zero.

Just as for the M_4 band, it is conceivable that the M_3 and M_3' bands originate from a spin-orbit admixture of the M_2 and M_2' levels with the ${}^3\Sigma_u^+$ level shown by the dotted line in Fig. 10. However, the strength of these transitions suggests that the assignment given is more likely.[32]

With the assumption that the M_4 band results from a spin-orbit admixture of the ${}^1\Sigma_u^+$ to the ${}^3\Pi_u$ level, it is not hard to determine the spin-orbit coupling parameter. Careful measurements of the intensities of the M_1 and M_4 bands were made. These proved to be in a ratio of 43.8 ± 3.0; most of the uncertainty arises from difficulty in determining the base line, as the M_4 band is not entirely resolved from M_2. Since the energy difference ΔE between the ${}^3\Pi_u$ and ${}^1\Sigma_u^+$ levels is about 0.41 eV, one finds from

$$H_{so}^2 \approx \Delta E^2/43.8$$

that $H_{so} = 0.062 \pm 0.003$ eV. This should be compared to the spin-orbit parameter of about 0.01 eV found by Mort *et al.*[34] for the F center in KCl. It is not clear why the F_2-center parameter should be this much larger.

VII. CONCLUDING REMARKS

A variety of techniques involving polarization modulation has been applied to the spectra of F_2 centers in KCl. The experiments described here are refinements and extensions of previous work on these centers. The results have provided more accurate polarization data on both singlet and triplet transitions. These data have permitted tentative identification of the symmetry of the wave functions of the excited levels upon which these transitions terminate.

For the future it would be very helpful to have energy-level calculations of the states of the hydrogen molecule out to an internuclear distance of at least 2.5 Å. In the present experiments the crystal was cleaved for convenience along the crystal axes; in investigations of F_2 centers it would be more useful to have a crystal cut along the [011], [0$\bar{1}$1], and [100] axes with F_2 alignment along [011]. In this way a direct and unambiguous separation of x-, y-, and z-polarized transitions would be obtainable. This would be most helpful in measuring the energies of the transitions terminating on Π states.

ACKNOWLEDGMENTS

Primary thanks are due Dr. Yves Farge, in whose laboratory I have been working on triplet-state problems. It was he who suggested that the optical deexcitation of the triplet state may be an important factor in inducing dichroism in the triplet band. I would also like to thank Robert Boyd for having supplied a copy of the hard-to-obtain article by Mulliken, and R. H. Silsbee for a number of helpful discussions.

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