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# Observation of singlet-triplet anticrossings in ${}^4\text{He}_2^*$

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Anticrossings between excited singlet and triplet levels of the  $\text{He}_2$  molecule have been observed. Measurements have been made on anticrossings which take place between the  $f(3d) {}^3\Delta_u$  and  $F(3d) {}^1\Delta_u$  states both in the  $v=0$ ,  $N=2,3,4$  and  $v=1$ ,  $N=2$  vibrational and rotational levels. Analysis of these results yields a new and more precise value for the excitation energy,  $T_0$ , from the  $a(2s) {}^3\Sigma$  to the  $A(2s) {}^1\Sigma$  state. This result, when combined with available optical data, fixes the absolute energy of all  $\text{He}_2$  excited states. The present experiment establishes that the steady state populations of the  ${}^3\Delta$  levels are greater than the  ${}^1\Delta$  levels under a variety of excitation conditions. Also, collisional transfer may take place before radiation giving rise to a given anticrossing signal appearing on optical emission lines of several nearby rotational levels.

## INTRODUCTION

In light atoms and molecules, the spin multiplicity quantum number (e.g., singlet, triplet, etc.) is very well conserved. This leads to a situation wherein, say, the entire triplet manifold's position is only imprecisely known relative to the singlet manifold which usually includes the ground state. Indeed, in the lightest molecules (e.g.,  $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{He}_2$ , etc.), optical intercombination bands are so highly forbidden that they have never been observed. Until recently, the only means available for the establishment of the triplets' absolute energies was the extrapolation of corresponding singlet and triplet states to the Rydberg limit. Such a method is inherently imprecise (compared to the optically determined relative energies within a manifold) and has led to discrepancies<sup>1,2</sup> in the absolute energy of the  $\text{H}_2$  triplet states of over  $100 \text{ cm}^{-1}$ .

Recently our two laboratories have developed<sup>2-4</sup> a new technique, the level anticrossing method, to determine the relative positions of singlet and triplet levels in He and  $\text{He}_2$ . In this method a spin ( $M_s = \pm 1$ ) component of the triplet state is tuned to essential degeneracy (the anticrossing point) with a singlet level by an external magnetic field. As the singlet and triplet levels are usually unequally populated, any perturbation between the levels causes changes in the intensity of optical emission from each level. The intensity change marks the anticrossing field and its value determines the zero-field separation of the singlet and triplet levels. The inherent precision of the anticrossing determination can be greater than the accuracy ( $\sim 0.01 \text{ cm}^{-1}$ ) claimed for the relative position of states within a manifold as determined from optical spectroscopy.

This paper describes the application of the anticrossing technique to the determination of the relative positions of the singlet and triplet states of the  $\text{He}_2$  molecule. The ground  $X {}^1\Sigma_g^+$  state of  $\text{He}_2$  is, of course, repulsive and therefore not suitable as a reference point. Ginter<sup>5</sup> is responsible for practically all of the recent optical work on  $\text{He}_2$ , and we follow (see Fig. 1) his

example of taking the  $N=v=0$  level of the  $a {}^3\Sigma_u^+$  state (the lowest bound state) as the zero of energy. The absolute energy of all other known states of  $\text{He}_2$  can be obtained from the optical spectra of Ginter and his tabulations, if the excitation energy  $T_0$  to the  $N=v=0$  level of the  $A {}^1\Sigma_u^+$  state is known. As no optical intercombination bands have been reported for  $\text{He}_2$ , Ginter has resorted to the method of extrapolation to the Rydberg limit to obtain  $T_0$ . The value of  $T_0$  so obtained<sup>5</sup> is  $2344.1 \text{ cm}^{-1}$  with a probable error of  $\sim 0.6 \text{ cm}^{-1}$ . Ginter notes, however, that this error estimate depends critically upon the assumed constancy of the quantum defects for the highest Rydberg states. Our analysis of

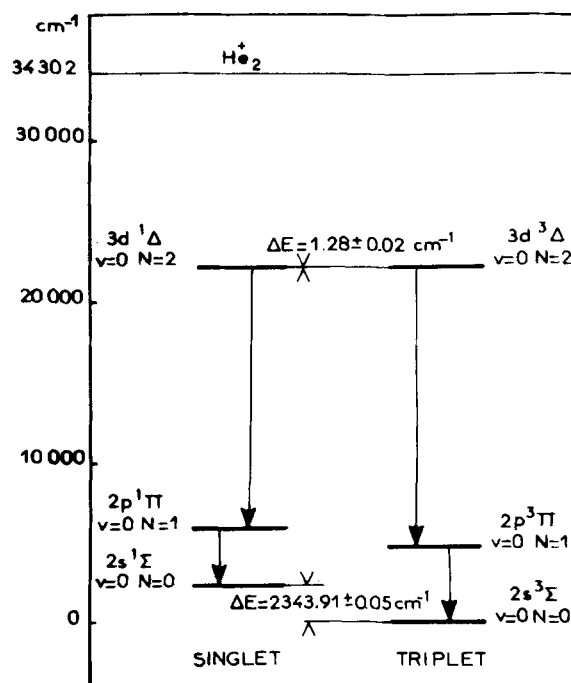


FIG. 1. Energy level diagram of  $\text{He}_2$  illustrating the positions of the states relevant to this investigation. Arrows indicate the optical transitions.

singlet-triplet anticrossings in  $\text{He}_2$  allows an independent and more precise determination of  $T_0$ .

## EXPERIMENTAL

The experiments reported in this paper were performed at the Service National des Champs Intenses (S.N.C.I.) at Grenoble (hereafter called Grenoble) and the Bell Telephone Laboratories, Murray Hill, NJ (hereafter denoted as BTL). The experiments were carried out essentially simultaneously and with two rather different apparatus. The results of the experiments are, however, entirely consistent, providing both redundant and complementary information. A brief description of each apparatus follows. Elsewhere in the text where the information is relevant and not self-evident, reference is made to indicate upon which apparatus the particular experiment was performed.

The apparatus at Grenoble is basically unchanged from that described in a previous report<sup>3</sup> of singlet-triplet anticrossings in  $\text{H}_2$ . Helium is enclosed in a sealed Pyrex cell at a pressure of  $\sim 10$  torr. The spectrum of  $\text{He}_2$  is excited by a microwave (2.45 GHz) discharge. The discharge cell is contained in a Bitter coil and the intensity and/or circular polarization of light emitted parallel to the magnetic field is monitored.

The equipment at BTL is basically unchanged from previous work.<sup>2,4</sup> To obtain the  $\text{He}_2$  spectrum, He, at 1–3 torr pressure, is bombarded by electrons from the source previously described. Significantly below this pressure the  $\text{He}_2$  optical spectrum disappears, and above this pressure the electron gun becomes unstable. Light intensity from a given optical emission line of  $\text{He}_2$  is monitored perpendicular to the magnetic field.

The apparatus at Grenoble and BTL are complemen-

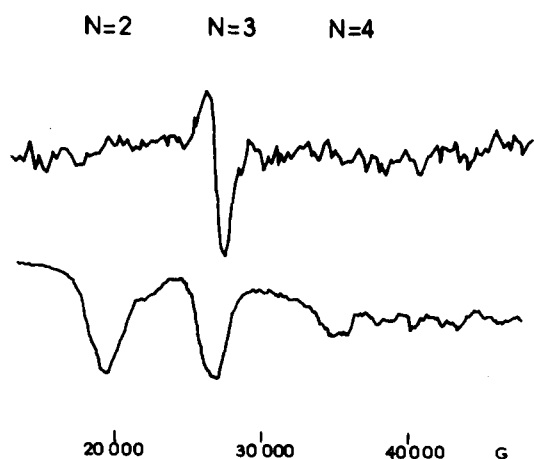


FIG. 2. Experimental trace taken at Grenoble of the  $\nu=0$ ,  $N=3$  anticrossing as monitored by the  $R2\ ^3\Delta$  emission line at  $5718\ \text{\AA}$ . The top trace is taken in circular polarization, while the lower trace is total intensity  $\parallel$  to the field. In the lower trace, besides the anticrossing signal from  $N=3$ , two other anticrossing signals appear for  $N=2$  and  $4$ . The position of these signals matched those found when the  $R1$  and  $R3$ , respectively, are monitored and are assumed introduced into  $R2$  emission by collisions. Notice that the signal in the polarization curve only occurs for the  $N=3$  anticrossing. Similar results were observed for the  $R1$ ,  $R3$ , and  $R4$  emission lines.

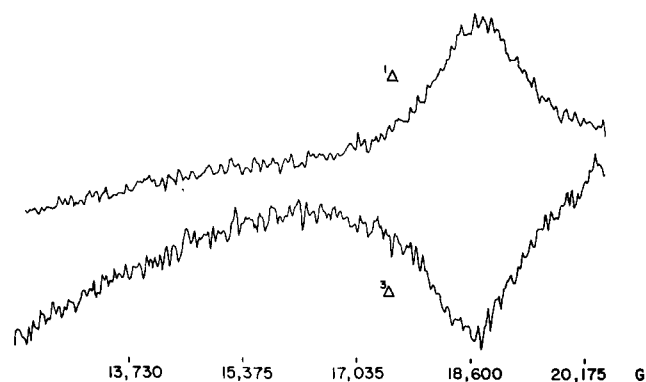


FIG. 3. Experimental trace taken at BTL of the  $\nu=1$ ,  $N=2$  anticrossing. The upper trace is obtained when the  $R1\ ^1\Delta$  emission line at  $6122\ \text{\AA}$  is monitored; the lower trace is obtained when the  $R1\ ^3\Delta$  emission line at  $5744\ \text{\AA}$  is monitored. In both cases, the quantity on the vertical axis is total intensity  $\perp$  to the field.

tary in many respects. The BTL magnet is limited to 2 T, while that at Grenoble can obtain 15 T. On the other hand, field stability of the Grenoble Bitter coil is  $\sim 1$  mT, while that of the BTL electromagnet is in the range of  $1\ \mu\text{T}$ . Measurements at BTL and Grenoble are at different pressures and under different excitation conditions. Also, the geometries are different, so that different polarization and angular effects may be studied.

## RESULTS—LINE POSITIONS

Representative experimental results from the Grenoble and the BTL laboratories are given in Figs. 2 and 3, respectively. Observations have been made at Grenoble for the  $N=2-4$ ,  $\nu=0$  levels of the  $f(3d)^3\Delta$  state of  $\text{He}_2$  using the  $R$ -branch lines. The observations at BTL have been on  $\nu=0$  and  $1$  for  $N=2$  of the  $f(3d)^3\Delta$  and  $F(3d)^1\Delta$  states via primarily the  $R1$  lines, but confirmatory observations have also been made on the  $Q2$  and  $P3$  lines.

The curves presented in Figs. 2 and 3 appear superficially rather different; however, both figures have essentially the same information content. To understand this, consider Eq. (1) of Ref. 2 or Eq. (3) of Ref. 6, which can be written as

$$H_0 = h\nu_0 / \mu_0 [g_S - g_N^t \Delta M_N - M_N^s \Delta g], \quad (1)$$

where

$$\Delta g = g_N^s - g_N^t,$$

$$\Delta M_N = M_N^s - M_N^t,$$

$h\nu_0$  = zero field separation of singlet minus triplet,

$g_S$  = free electron  $g$  factor (2.00232),

$g_N^{t(s)}$  = effective orbital angular momentum  $g$  factor of the  $N$ th level of the triplet (singlet) state,

and

$H_0$  = anticrossing field.

In writing Eq. (1) we have assumed that second order

TABLE I. Summary of experimental anticrossing results for  $\text{He}_2$ . Field positions are given in milliteslas (1 mT=10 G).

$N =$	2	3	4	2
$v =$	0	0	0	1
$g_N^t$ <sup>a</sup>	$0.615 \pm 0.015$	$0.278 \pm 0.010$	$0.136 \pm 0.006$	...
$\Delta H$ (mT)	$40 \pm 33$	$35 \pm 10$	$25 \pm 10$	$31 \pm 14$
$g_N^s$ <sup>b</sup>	$0.593 \pm 0.026$	$0.255 \pm 0.015$	$0.120 \pm 0.010$	$g_N^t - 0.018$
$g_N^t$ (theor) <sup>c</sup>	0.646	0.290	0.142	0.649
$g_N^s$ (theor) <sup>c</sup>	0.640	0.277	0.128	0.644
Anticrossing center (mT)	$1954^d \pm 13$	$2645^e \pm 16$	$3358^e \pm 18$	$1848^d \pm 8$
Position <sup>f</sup> of $M_S = 0, M_N = 0 \leftrightarrow M_S = 1, M_N = -1$ (mT)	$1980 \pm 17$	$2650 \pm 17$	$3363 \pm 19$	$1868 \pm 13$
Total width <sup>g</sup> (mT)	$169 \pm 40$	$193 \pm 30$	$236 \pm 30$	$125 \pm 15$
$h\nu_0$ (This work) ( $\text{cm}^{-1}$ )	$1.28 \pm 0.02$	$2.13 \pm 0.02$	$2.93 \pm 0.02$	...
$h\nu_0$ (Ginter) ( $\text{cm}^{-1}$ )	1.49	2.30	3.12	1.31
Difference ( $\text{cm}^{-1}$ )	-0.21	-0.17	-0.20	...

<sup>a</sup>Measured from optical Zeeman effect.

<sup>b</sup>Determined from  $g_N^t$  and  $\Delta g$ .

<sup>c</sup>Values calculated from case *b* and perturbation theory including only  $3d \Pi-\Delta$  interaction.

<sup>d</sup>As measured in total intensity  $\perp$  to field on  $R1 \ ^3\Delta$  emission.

<sup>e</sup>As measured in total intensity  $\parallel$  to field on the  $R$ -branch  $\ ^3\Delta$  emission.

<sup>f</sup>Calculated from the  $\Delta H$  determination.

<sup>g</sup>Measured for  $R$ -branch line, except  $v=0, N=2$  for the  $Q2$  line.

Zeeman effects and fine structure are unimportant. While not exact, this is a reasonable approximation. We also assume the singlet states lie above the triplet states as Ginter's  $T_0$  predicts and as can be verified by the internal consistency of our results.

For any molecule without nuclear spin, the combined space fixed projection ( $M_N + M_S$ ) must be conserved for any internal perturbation. The spin-orbit interaction couples the singlet and triplet states with selection rules  $\Delta M_N = -\Delta M_S = \pm 1$ . As the singlet lies above the triplet, only the  $M_S = 1$  level of the triplet can anticross and we have  $\Delta M_N = 1$ . Thus, Eq. (1) implies that between states of a given  $N$ , there are actually  $2N$  anticrossings of the Zeeman components with  $M_N^s = N, N-1, \dots, 1-N$ .

According to the above model, the  $2N$  Zeeman level anticrossings are separated from each other by an amount determined by  $\Delta g$ . If this amount is considerably less than the intrinsic anticrossing width, only one blended line will be observed.

However, as each of the Zeeman components carries unique polarization characteristics, the actual line shape is a sensitive function of the means of detection. This is actually a very useful result. Equation (1) can be seen to contain three unknown parameters,  $g_N^t$ ,  $\Delta g$ , and  $h\nu_0$  ( $g_S$  can be taken to be the free spin  $g$  factor without introducing any error). The orbital  $g$  factor of

the triplet,  $g_N^t$ , has been measured independently from the optical Zeeman effect at 6 and 12 T. These values are listed in Table I. Similar experiments on the singlet emission lines were not possible owing to the weakness of the lines.

Since  $\Delta g$  is small compared to  $(g_S - g_N^t)$ , Eq. (1) predicts each observed anticrossing to be  $2N$  lines, separated in field by an approximate constant  $\Delta H$ . However, as noted above, the relative strength of the various contributions is strongly dependent upon the detection scheme. Figure 4 illustrates via a stick diagram the expected intensity (for the simplest case,  $N=2$ , an  $R1$  emission line) for the three experimental detection schemes. In principle, the shift in the apparent center position of any anticrossing obtained by any pair of detection schemes gives a value of  $\Delta H$ .

In the work performed at BTL, it was easiest to measure the anticrossings in total intensity  $\perp$  to the field. Measurements of the  $R1$  lines for both the  $\ ^1\Delta$  and  $\ ^3\Delta$  lines allowed a rough determination of  $\Delta H$  for the  $N=2$  states,  $v=0$  and 1. Expanding Eq. (1) for  $\Delta H/H \ll 1$ ,  $\Delta g$  can be determined by the relationship

$$\Delta H \approx H_0 [\Delta g / (g_S - g_N^t)], \quad (2)$$

where  $H_0$  can be taken as the singlet (or triplet) anticrossing position with negligible error.

In the Grenoble experiments, the difference in posi-

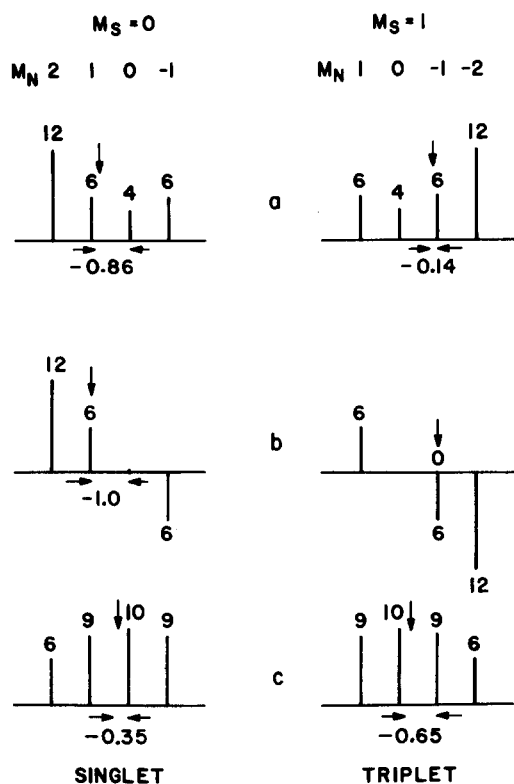


FIG. 4. Stick diagram illustrating the components contributing to the observed line in the simplest case  $N=2$ . The figure is drawn assuming  $g_N^t > g_N^s$  and that the singlet lies above the triplet. The three sets of diagrams are appropriate for R1 emission for the three experimental arrangements. In (a), the quantity monitored is total intensity  $\parallel$  to the field; in (b), circular polarization ( $\sigma^+ - \sigma^-$ ), and in (c), total intensity  $\perp$  to the field. The blended line center is indicated by an arrow and its shift in terms of  $\Delta H$ , the separation between components, given from the  $M_S=M_N=0 \leftrightarrow M_S=1, M_N=-1$  component.

tion of anticrossing curves obtained in total intensity (parallel to the field) and the circular polarization curve ( $\sigma^+ - \sigma^-$ ) for the  $^3\Delta$  emission was used for the  $\Delta H$  determination on the  $N=3$  and 4 levels. Table I lists the combined results of the experiments. The  $g$  factors for both singlet and triplet levels are given as obtained from the optical Zeeman experiment and the  $\Delta g$  measurement. The center of the  $^3\Delta$  anticrossing curve seen in total emission is given as well as the position of the  $M_S=0, M_N=0 \rightarrow M_S=1, M_N=-1$  component as deduced from the  $\Delta H$  measurements. From the latter number, the singlet-triplet separation  $h\nu_0$  is calculated directly using Eq. (1). In the last rows these values are compared with those computed from Ginter's value<sup>5</sup> of  $T_0$ . It is clear that a small correction to the optical  $T_0$  is needed. The best value of  $T_0$  is found to  $2343.91 \pm 0.05 \text{ cm}^{-1}$ . This value can be seen to be within the error limits expected by Ginter<sup>5</sup> for his value of  $T_0$  and more than 10 times as precise.

## RESULTS—INTENSITIES AND WIDTHS

Perhaps the most striking qualitative observation concerning the  $\text{He}_2$  anticrossings is the fact that the intensity of optical emission in the triplet bands decreases at the anticrossing point while the singlet increases. In

previous  $\text{H}_2$  and  $\text{He}$  experiments, the opposite condition prevailed, as expected from the larger cross sections for excitation of singlets by electron impact. There seems no clear-cut reason in  $\text{He}_2$  for the effective singlet and triplet excitation cross sections to differ. The  $\text{He}_2$  formation process is fairly complicated but probably involves<sup>7,8</sup> associative ionization  $\text{He} + \text{He}^*$  to form the  $\text{He}_2^+$  ion. The ion then is neutralized via a three-body collision with two electrons to form the  $F^1\Delta$  or  $f^3\Delta$  state.

However, as is physically obvious and mathematically stated in Eq. (1) of Ref. 4, differences in excited state lifetimes are sufficient to create steady state population differences and hence anticrossing signals, even with equal excitation cross sections. In  $\text{H}_2$  and  $\text{He}$  all the states observed in anticrossings thus far have comparable lifetimes. In the case of  $\text{He}_2$ , the singlet state can radiate not only in the visible (the lines monitored) as does the triplet, but also has an allowed<sup>9</sup> vacuum ultraviolet transition to the repulsive ground state. In the  $\text{H}_2$  molecule, lifetimes for excited singlets radiating to the ground state are of the order of 1 nsec, while those not radiating to the ground state are typically tens of nsec, the difference of course being basically attributable to the  $\nu^3$  factor in the Einstein coefficient. It thus may be that the singlet state is considerably shorter lived than the triplet.

A second matter of considerable qualitative importance is clearly demonstrated in Fig. 2. It shows that at higher pressures ( $\sim 10$  torr) one observes anticrossing signals due to collisional transfer between rotational levels within the triplet (or singlet) manifold before radiation. Interestingly, these collision-induced anticrossing signals appear only in total intensity, not polarization. This loss of polarization can occur during the collision process itself which transfers the molecule from the particular  $N, M_N$  levels which undergo the anticrossing at the studied field, to another  $N', M'_N$  level which is observed, indicating that the probability of transition from a particular  $M_N$  to all the  $M'_N$  is roughly equal, owing to the isotropy of the collision process. There can also be destruction of orientation by subsequent collisions while the molecule is in the final  $N'$  level. But this disorientation process is also present in the original  $N$  level, inducing redistribution between  $M_N$  levels and hence a diminution of the ratio of polarization vs intensity anticrossing signals. If the individual  $M_N$  levels were optically isolated we would observe, on a particular  $M_N$  level, anticrossings coming from the other  $M_N$ . The lack of polarization signals in  $N'$  is presumably due to the transfer  $N \rightarrow N'$  during collision process. On the other hand, there are apparently no strong selection rules in this rotational transfer.<sup>10,11</sup> Only initial observations have been made of both effects and future experiments are planned.

Finally, we observe that in the limit that the perturbation is much stronger than the lifetime broadening, which certainly pertains to the present case, the linewidth (listed in Table I) is directly proportional to the perturbation strength. As has been pointed out earlier, the observed lines are actually composed of a number

of components of varying intensity. However, as the positions of the individual components have already been determined, in principle it is a simple matter to determine the components' widths.

However, in practice, the relatively large errors in  $\Delta H$  give rise to not particularly accurate values for the component linewidths obtained from a computer simulation of the observed line. Generally the  $M_N = M_S = 0 \leftrightarrow M_S = 1, M_N = -1$  component's width is  $\sim 30\% - 90\%$  of the observed width. However, even if there were little experimental error in the linewidth determination, obtaining an accurate value for the matrix element of the spin-orbit perturbation between the  ${}^1, {}^3\Delta$  states would still be difficult. The standard formula<sup>4,6</sup> for the strong perturbation limit includes a factor  $f_r$  which depends upon the relative lifetimes of the states involved, which are unknown. Thus it is probably imprudent to do more than estimate from the observed width that the electronic spin-orbit matrix element is of the order of a GHz. The result can be compared to the value of  $\sim 200$  MHz calculated from a hydrogenic approximation for the diagonal  $3d\ {}^3\Delta$  spin-orbit coupling constant. This relatively large increase in size of the off-diagonal spin-orbit perturbation compared to the diagonal one is consistent with previous anticrossing results<sup>2-4</sup> in  $\text{H}_2$  and He.

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<sup>1</sup>W. Kolos, Chem. Phys. Lett. **1**, 19 (1967).

<sup>2</sup>T. A. Miller and R. S. Freund, J. Chem. Phys. **61**, 2160 (1974).

<sup>3</sup>R. Jost and M. Lombardi, Phys. Rev. Lett. **33**, 53 (1974).

<sup>4</sup>T. A. Miller, R. S. Freund, F. Tsai, T. J. Cook, and B. R. Zegarski, Phys. Rev. A **9**, 2474 (1974).

<sup>5</sup>M. L. Ginter, J. Chem. Phys. **42**, 561 (1965); M. L. Ginter and D. S. Ginter, *ibid.* **48**, 2284 (1968); M. L. Ginter and R. Battino, *ibid.* **52**, 4469 (1970); M. L. Ginter, *ibid.* **45**, 248 (1966); M. L. Ginter, J. Mol. Spectrosc. **17**, 224 (1965); M. L. Ginter, *ibid.* **18**, 321 (1965). See also the review on  $\text{He}_2$  in *Molecules Diatomiques Données Spectroscopiques* (Hermann, Paris, 1973).

<sup>6</sup>T. A. Miller and R. S. Freund, J. Chem. Phys. **63**, 256 (1975).

<sup>7</sup>A. B. Callear and R. E. M. Hedges, Trans. Faraday Soc. **66**, 2921 (1970).

<sup>8</sup>W. Lichten, M. V. McCusker, and T. L. Vierima, J. Chem. Phys. **61**, 2200 (1974).

<sup>9</sup>The transition in the uv is  $F\ {}^1\Delta_u \rightarrow X\ {}^1\Sigma_g^+$ , which is forbidden for case *b* coupling by the  $\Delta\Lambda = 0, \pm 1$  selection. However, *L* uncoupling is certainly present, and this selection rule is of limited applicability. Indeed, the corresponding visible transition  $f\ {}^3\Delta_u \rightarrow c\ {}^3\Sigma_g^+$  is well known.

<sup>10</sup>P. W. Daly and T. Oka, J. Chem. Phys. **53**, 3272 (1970).

<sup>11</sup>K. Bergmann and W. Demtröder, J. Phys. B **5**, 1386 (1972).