

Crystal Spectra of Chromium trisAcetyl Acetone

Animesh Chakravorty and Sadhan Basu

Citation: *The Journal of Chemical Physics* **33**, 1266 (1960); doi: 10.1063/1.1731381

View online: <http://dx.doi.org/10.1063/1.1731381>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/33/4?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Optical emission spectra of chromium doped nanocrystalline zinc gallate](#)

J. Appl. Phys. **106**, 063721 (2009); 10.1063/1.3224866

[Rotationally resolved spectra of jet-cooled VMo](#)

J. Chem. Phys. **127**, 014311 (2007); 10.1063/1.2747617

[Nonradiative processes in transition ions in crystals](#)

Rev. Sci. Instrum. **74**, 312 (2003); 10.1063/1.1515903

[Photolysis of Acetone in the Presence of HI and the Decomposition of the Acetyl Radical](#)

J. Chem. Phys. **36**, 2196 (1962); 10.1063/1.1732851

[Pyrolysis of Acetone and the Heat of Formation of Acetyl Radicals](#)

J. Chem. Phys. **23**, 2310 (1955); 10.1063/1.1740745



Br_2 , I_2 and At_2 . This indicates that $D(\text{F}_2)$ and $D(\text{F}_2^+)$ are both lower than might be expected from the trends of this family, but that all four quantities of Eq. (3) for $X=\text{At}$, namely $D(\text{At}_2^+) = 2.4$ eV, $D(\text{At}_2) = 1.2$ eV, $I(\text{At}) = 9.5$ eV, and $I(\text{At}_2) = 8.3$ eV, appear to be reasonable estimations.

¹ W. Finkelnburg and F. Stern, *Phys. Rev.* **77**, 303 (1950).

² G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), 2nd ed., pp. 512-541.

³ Y. P. Varshni, *Z. Physik*, **135**, 512 (1953).

⁴ J. T. Herron and V. H. Dibeler, *J. Chem. Phys.* **32**, 1884 (1960).

⁵ K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957).

⁶ A. G. Gaydon, *Dissociation Energies*, (Chapman and Hall, Ltd., London, 1953), pp. 222-226.

⁷ T. L. Cottrell, *The Strengths of Chemical Bonds*, (Butterworths Scientific Publications, Ltd., London, 1954), pp. 282-288.

⁸ C. E. Moore, *Natl. Bur. Standards (U. S.) Circ. No. 467*, 3 (1958).

Crystal Spectra of Chromium *tris*-Acetyl Acetone

ANIMESH CHAKRAVORTY AND SADHAN BASU

Department of Chemistry, University College of Science & Technology, Calcutta 9, India

(Received June 2, 1960)

IN chromium *tris*-acetyl acetone the cubic crystal field is expected to split the fivefold degenerate d orbitals into two levels of symmetry, e_g and t_{2g} , respectively, the optical transition between which will give rise to one absorption band. It was observed by Mead¹ that the visible absorption band of hexacoordinated trivalent chromium complexes could be very well represented by Lowry-Hudson's Gaussian curve, suggesting that only one electronic transition is responsible for the absorption band, as expected from the theoretical considerations. Recently Jarrett² from the paramagnetic resonance measurements on chromium *tris*-acetyl acetone concluded that, in this case at least, in addition to the normal cubic field a trigonal field is present which causes a further splitting of the t_{2g} levels into a doublet and a singlet. Although the splitting is not as large as claimed by Jarrett, it is sufficient to give rise to two absorption bands with different polarization.³ In Fig. 1 are shown the absorption spectra of a crystal of chromium *tris*-acetyl acetone with light polarized parallel and perpendicular to the long axis of the crystal.⁴ It is evident that we do get two bands with peaks at $555 \text{ m}\mu$ and $585 \text{ m}\mu$ which are differently polarized. Each band can be approximately represented by a suitable Lowry-Hudson relation, suggesting that each one is associated with one transition only.

Jarrett suggested that the trigonality may arise from the π bonding of the metal d electron with the p electron of the ligand oxygen. This interpretation is probably correct because the $275 \text{ m}\mu$ band of acetyl acetone is

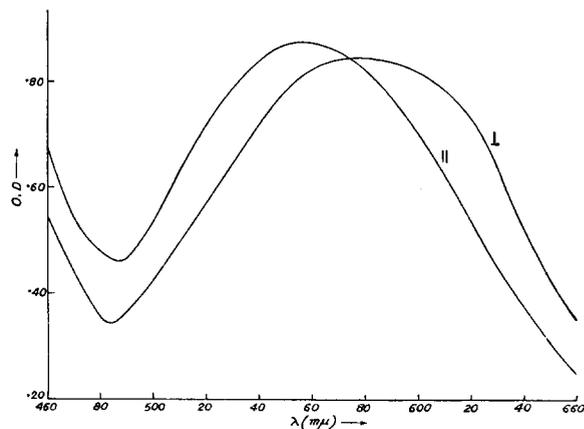


Fig. 1

shifted to $335 \text{ m}\mu$ in chromium *tris*-acetyl acetone⁵ which may be due to mesomeric interaction of the metal-oxygen π bond with the conjugated double bonded system of the ligand molecule.

Sincere thanks are due to Dr. L. E. Orgel, Cambridge, for helpful suggestions.

¹ A. O. Mead, *Trans. Faraday Soc.* **30**, 1052 (1934).

² H. S. Jarrett, *J. Chem. Phys.* **27**, 1298 (1957).

³ L. Orgel, private communication.

⁴ A. Chakravorty and S. Basu, *Nature* **184**, 50 (1959); **185**, 681 (1960).

⁵ S. Basu and K. K. Chatterjee, *Z. physik Chem.* **209**, 360 (1958).

Hyperfine Structure of F -Center Spin Resonance in Sodium Azide

F. F. CARLSON, G. J. KING, AND B. S. MILLER

Basic Research Group, U. S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia

(Received June 14, 1960)

THE electron spin resonance absorption line of an F center is normally a broad, smooth, Gaussian line.^{1,2} An important type of broadening which occurs in an F -center resonance is produced by unresolved interactions of the F -center electron with the magnetic hyperfine fields of the nuclei surrounding the F -center site.

The hyperfine structure in the spin resonance line cannot be resolved in the standard electron spin resonance experiment unless special conditions exist. Among these conditions are: the value $|\psi_F|^2$ of the F -center wave function ψ_F at the nuclei of the nearest cations must be large, and the magnetic hyperfine field of these nuclei must be sufficiently strong to overcome competing broadening effects, including the hyperfine fields of other nuclei. Since these conditions are not usually realized, the electron nuclear double-resonance techniques³ are used to study hyperfine interactions.

On rare occasions, F -center resonances have been observed in which the hyperfine structure has been resolved by standard techniques.^{4,5} In this present work we report an ultraviolet irradiation-induced microwave resonance absorption in NaN_3 which we conclude is caused by F centers. The resonance displays the characteristic hyperfine structure of the F center observed by Lord in NaF .⁵ The optical absorption data for irradiated NaN_3 corroborates the conclusion that the center is of the F type.⁶

Microcrystalline NaN_3 was sealed in an evacuated fused silica tube and then irradiated at 90°K with an ultraviolet lamp (Hanovia S100). The material turned from white to blue during this treatment. Cunningham and Tompkins⁶ have shown that the ultraviolet irradiation of NaN_3 at 90°K produces F -type optical absorption bands but not V -type optical absorption bands.

The sample was examined at 90°K in a Varian EPR spectrometer and an absorption spectrum of 19 evenly spaced lines was found. The shape of the envelope of the lines was Gaussian in nature and showed saturation effects. The g values for the lines were distributed closely above and below $g=2$.

We interpret this spectrum in terms of an N_3^- vacancy model analogous to de Boer's model for an F -center in an alkali halide. Electrons freed during ultraviolet irradiation are trapped at N_3^- vacancies, which are present in large numbers. The immediate environment of the F electron in the N_3^- vacancy consists of six equivalent nearest neighbor sodium ions with nuclear spin $\frac{3}{2}$. The interaction of this F electron with the magnetic field of the six sodium nuclei should split the F resonance into 19 lines. Using broad field sweep and high gain on the EPR spectrometer, 19 lines are actually observed. Figure 1 shows a trace made at lower sweep and gain for presentation purposes.

The analysis of Lord,⁵ which assumed that the magnetic hyperfine field effect of the nearest neighbors of the F electron is much greater than that of other ionic shells, is adopted here. The broadening of the individual lines is ascribed in part to the action of nuclear hyper-

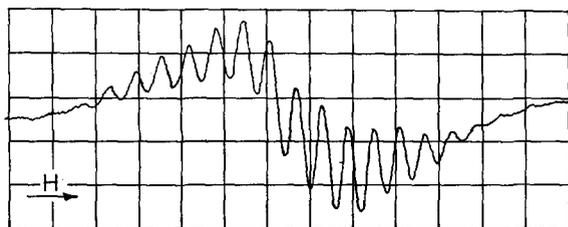


FIG. 1. The slope, dx''/dH , of the electron-spin-resonance absorption in sodium azide at 9000 Mc/sec and 3000 gauss. The separation of the hyperfine lines is 9.1 gauss.

fine fields of other shells of ions. Numerical computations and measurements are given in Table I.

The interest and encouragement of Z. V. Harvalik are gratefully acknowledged.

¹ A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* **91**, 1066 (1953).

² A. M. Portis, *Phys. Rev.* **91**, 1071 (1953).

³ G. Feher, *Phys. Rev.* **105**, 1122 (1957).

⁴ N. W. Lord and C. K. Jen, *Bull. Am. Phys. Soc.* **1**, 12 (1956).

⁵ N. W. Lord, *Phys. Rev.* **105**, 756 (1957).

⁶ J. Cunningham and F. Tompkins, *Proc. Roy. Soc. (London)* **A251**, 27 (1959).

The Effective Ionic Charge in CdS^*

FREDERIC KEFFER†

*Department of Physics, University of California,
Berkeley 4, California*

(Received June 20, 1960)

SINCE no precise elastic or piezoelectric data on any of the wurtzite-type binary compounds have been available, a quantitative check of the macroscopic theory of the distortion and polarization of these compounds¹ has not hitherto been possible. Recent measurements of the elastic² and piezoelectric³ constants of CdS , however, now allow a partial verification of the theory and also an estimate of the size of the postulated charge $\pm e$ per ion.

The pertinent data are, for CdS ,

$$(2s_{13} - s_{11} - s_{12}) = -3.1302 \times 10^{-12} \text{ cm}^2/\text{dyne},$$

$$(s_{33} - s_{13}) = 3.2591 \times 10^{-12} \text{ cm}^2/\text{dyne},$$

$$(d_{33} - d_{13}) = \pm 12.3 \times 10^{-8} \text{ esu/dyne}.$$

Unfortunately the signs of the piezoelectric constants are not easily determined. We have assumed, with Tanaka and Tanaka, opposite signs for d_{33} and d_{13} .

When these numbers are inserted into Eq. (21a) of footnote reference 1, the following relation is obtained:

$$\frac{(c/a) - (c_0/a_0)}{(c_0/a_0)} = -0.0089 f^2 \pm 0.0014 f. \quad (1)$$

It is to be noted that the second term on the right (piezoelectric distortion) is about ten times larger than

TABLE I. Experimental data and results.

Microwave frequency	≈ 9000 Mc/sec
Magnetic field	≈ 3000 gauss
Central g value	2.003 ± 0.001
Separation of hyperfine structure (Hyperfine field of sodium shell)	9.1 ± 0.1 gauss
$ \psi_F ^2$ at sodium nucleus	$1.45 \times 10^{23} \text{ cm}^{-3}$
Hyperfine field of next effective shell From linewidth of structure	2.3 ± 0.3 gauss
Crystal structure of NaN_3	Rhombohedral
Temperature of sample during entire experiment	90°K