

It should also be pointed out that the twist (about the carbon-carbon double bond) reported by the electron diffraction investigators¹ is not minor but of the order of 40° or so, and hence the molecule should have significant asymmetry if their results are correct. These Raman data are not compatible with such asymmetry and hence support the planar structure reported by the microwave workers.³ The Raman investigation merely favors one structure over another; the really interesting work lies in determining the root of the discrepancy. The Raman and microwave techniques should favor each other since they give more specific information on molecular symmetry and they are relatively passive methods. Whether the current disagreements can be traced to some experimental effects or in data treatment remains to be seen.

It should be mentioned that after the submission of this paper for publication it was pointed out^{1,3} that other related molecules may also exhibit this twisted configuration as determined by electron diffraction. Through the kindness of Professor Bauer, who supplied the samples, we have examined the Raman spectra of $\text{CH}_2=\text{CHCF}_3$ and *cis*- and *trans*- $\text{CF}_3\text{CF}=\text{CFCF}_3$. The results of these measurements indicate the presence of several depolarized lines and therefore it may be con-

cluded that all of these molecules, like perfluoropropene, possess the planar, undistorted structure.

We should like to thank Professor Ellis Lippincott and Mr. Ronald Ace for the use of the Raman facilities at the University of Maryland and for assistance in making the measurements. In addition we should also like to thank Dr. James Willis and Dr. P. Robert Reed of Cary Instruments and Spex Industries, respectively, for their effort in obtaining the Raman spectra of $\text{C}_3\text{H}_3\text{F}_3$ and C_4F_8 molecules. We are also indebted to Professor Bauer and Dr. Lide for interesting discussions regarding the structure of these molecules.

* NRC-NRL Resident Research Associate.

¹ S. H. Bauer and C. H. Chang, Abstracts 161st Meeting American Chemical Society, Los Angeles, Cal., 28 March 1971, Paper Phys. 14., and private communications.

² F. A. B. Buck and R. L. Livingston, J. Am. Chem. Soc. **70**, 2817 (1948); J. Chem. Phys. **18**, 570 (1950).

³ E. J. Jacob and D. R. Lide, Jr., Abstracts 26th Symp. Mole. Struct. Spectry., Columbus, Ohio, 14 June 1971, Paper B2, and private communication.

⁴ J. R. Nielsen, H. H. Claassen and D. C. Smith, J. Chem. Phys. **20**, 1916 (1952).

⁵ The only references to the torsion are the microwave investigation (Ref. 3) and an unsuccessful attempt to observe it in the far infrared. See, K. R. Loos, Ph.D. thesis, Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass., 1964.

On the Electron Affinity of Fluorine

RICHARD MILSTEIN AND R. STEPHEN BERRY

Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 15 June 1971)

Although the electron affinity of fluorine has been considered reasonably well known for some time, there is a discrepancy in the literature that needed to be resolved.¹ Berry and Reimann² observed the photo-detachment continuum of F^- in the absorption spectra of shock-induced dissociation products of CsF , RbF , and KF , and reported two thresholds, at 3595 and 3542 Å. More recently, Popp^{3,4} has looked at the same continuum in emission, using arcs containing SF_6 and BF_3 . He finds thresholds at 3646 and 3595 Å. In both sets of experiments the interval between the thresholds corresponds very well to the 404-cm^{-1} splitting of the $^2P_{3/2}$ and $^2P_{1/2}$ final states of neutral F. Presumably the 3595-Å thresholds seen by Popp and by Berry and Reimann are the same. The problem was to determine whether it was the higher-energy threshold, as indicated by Popp, or the lower-energy threshold, and therefore the electron affinity, as claimed by Berry and Reimann.

We have restudied the absorption spectra of the fluoride salts, using a shock technique^{5,6} considerably refined from the methods of Berry and Reimann. The time-resolved spectra of shock-dissociated CsF and

RbF obtained this way show a distinct threshold at 3649 ± 2 Å. The measurements were made from high-contrast enlarged prints of the spectra. This threshold corresponds to an electron affinity for the fluorine atom of 3.398 ± 0.002 eV, clearly in agreement with Popp's value of 3.400 ± 0.002 eV. The previously reported weak threshold² at 3542 Å was not observed in this work. The only substantive difference between the present work and that of Berry and Reimann, apart from the time resolution of the present work, was the presence of aluminum foil supporting material in the work of Berry and Reimann. We infer that this "threshold," if it is real, is probably due to some species involving Al and F. In fact, there is a known system of violet-degraded bonds of AlF at 3450–3720 Å.⁷ It should be recognized, however, that the error bars in the spectra of Berry and Reimann are large enough to admit the possibility that the 3542-Å "threshold" is actually plate noise. This is not the case with the very distinct step at 3594 Å.

¹ R. S. Berry, Chem. Rev. **69**, 533 (1969).

² R. S. Berry and C. W. Reimann, J. Chem. Phys. **38**, 1540 (1963).

³H.-P. Popp, Z. Naturforsch. 20a, 642 (1965).

⁴H.-P. Popp, Z. Naturforsch. 22a, 254 (1967).

⁵R. S. Berry, T. Cernoch, M. Coplan, and J. J. Ewing, J. Chem. Phys. 49, 127 (1968).

⁶J. J. Ewing, R. Milstein, and R. S. Berry, J. Chem. Phys. 54, 1752 (1971).

⁷H. C. Rowlinson and R. F. Barrow, Proc. Phys. Soc. London A66, 437 (1953).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 55, NUMBER 8 15 OCTOBER 1971

Electron Paramagnetic Resonance of Chromia Supported on Silica. Enhancement of Dispersed Chromia by Oxalic Acid Complexing*

D. E. O'REILLY

Argonne National Laboratory, Argonne, Illinois 60439

AND

J. E. SALAMONY† AND R. G. SQUIRES

Purdue University, West Lafayette, Indiana 47907

(Received 25 March 1971)

Several distinct states of chromia adsorbed on high surface area alumina have been detected by electron paramagnetic resonance techniques.^{1,2} On the material reduced in hydrogen at 500°C at low concentrations magnetically isolated Cr³⁺ ions predominate (δ phase) and at higher concentrations clusters of Cr³⁺ ions occur (β phase) which are antiferromagnetic with a distribution of effective Curie temperatures.^{1b} In the current work we have studied these resonances versus concentration and temperature for chromia supported on silica and have found a convenient method of greatly enhancing the δ -phase resonance by complexing the impregnating chromia solution with oxalic acid and subsequently oxidizing away the complexed oxalic acid.

High area silica gel (BET area = 210 m² g⁻¹) was impregnated with a solution of CrO₃ in water, dried at 250°C, and reduced in hydrogen at 500°C. As had been previously reported² and contrary to what had been stated in the literature,^{1d} the δ -phase resonance was observed in the reduced materials. The intensity of the δ -phase resonance attains a broad maximum near 0.1 wt% Cr and decreases with further increase in chromium concentration. Such behavior is in sharp contrast to that observed for the impregnated chromia-alumina system^{1b} where the maximum in δ -phase intensity occurs near 2 wt% Cr. By means of the Kramers-Kronig relation³ the number of spins contributing to the β -phase resonance may be obtained by integration of the EPR derivative signal. The width ΔH of the β -phase resonance is large ($\Delta H > 500$ G), but the error involved in assuming the number of spins to be proportional to the doubly integrated absorption derivative is less than 10% for widths below 1000 G. This may be demonstrated by exact evaluation of the Kramers-Kronig relationship for a Lorentzian lineshape by complex integration. The doubly integrated intensity of the β -phase resonance for a sample containing 0.35 wt% Cr is shown in Fig. 1.

The EPR intensity below 100°C increase with increase in temperature, reaches a maximum near 100°C and, with further increase in temperature, decreases as for a normal paramagnetic material. This behavior is similar to that observed for the impregnated chromia-alumina system^{1b} and results from the antiferromagnetic coupling of neighboring Cr³⁺ spins of β -phase clusters. For α -Cr₂O₃ a sharp increase in EPR intensity is observed near 30°C as had been reported earlier.^{1a,1b} As demonstrated in a recent quantum-mechanical calculation,⁴ the width and shape of the β -shape resonance is accounted for by the presence of nearest neighbor pairs of Cr³⁺ ions and higher clusters. Earlier it had been suggested^{1b,4} that the isolated Cr³⁺ pairs did not contribute to the β -phase resonance.

Oxalic acid forms a very stable 3:1 complex ion with Cr³⁺ in aqueous solution.⁵ The complex ion is relatively large and should prevent β -phase clusters from forming prior to oxidizing the material at 500°C with oxygen. After oxidation, a sample containing 0.43 wt% Cr was reduced in hydrogen at 500°C as with previous samples. The EPR signal at -160°C con-

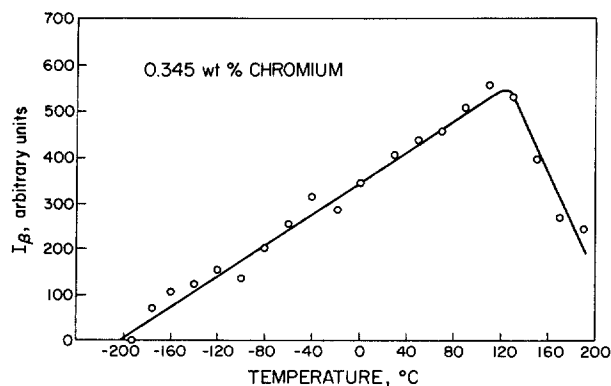


FIG. 1. Doubly integrated intensity of the β -phase resonance (I_{β}) of 0.35 wt% Cr on silica gel versus temperature.