

AD-753 380

ELECTRONIC SPECTRA AND STRUCTURE OF
LARGE MOLECULES AND CRYSTALS

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Prepared for:

Army Research Office (Durham)

1972

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UNCLASSIFIED

Security Classification

AD-753380

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
University of Pennsylvania		Unclassified	
		2b. GROUP	
		NA	
3. REPORT TITLE			
Electronic Spectra and Structure of Large Molecules and Crystals			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Final Report: 1 July 1966 - 30 Jun 1969			
5. AUTHOR(S) (First name, middle initial, last name)			
Robin M. Hochstrasser			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	
1972		x 6	
6a. CONTRACT OR GRANT NO.		6b. ORIGINATOR'S REPORT NUMBER(S)	
DA-31-124-ARO-L-466		NA	
b. PROJECT NO.			
c.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		6455.6-C	
10. DISTRIBUTION STATEMENT			
Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		U. S. Army Research Office-Durham Box CM, Duke Station Durham, North Carolina 27706	
13. ABSTRACT			
The first detailed study of the electronic spectrum of benzophenone crystals was completed. The triplet state at 24187 cm^{-1} was characterized as $n\pi^*$ and shown to be the analogue of the formaldehyde lowest triplet state. We showed that at least two of the spin substates are radiatively Studies of the low temperature spectra of a number of ketones showed perturbations, in the form of line broadening, that could be used to expose higher excited states of many molecules. The difference in linewidths for the singlet and triplet states of benzophenone was used to determine a value of ca. 10^{11} sec^{-1} for the intersystem crossing rate constant			
14. KEY WORDS		Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U S Department of Commerce Springfield VA 22151	
Benzophenone Crystals			
Ketones			
Electronic Spectra			
Large Molecules			
Crystals			

DD FORM 1473
1 NOV 65REPLACES DD FORM 1473, 1 JAN 64, WHICH IS
OBSOLETE FOR ARMY USE.

Unclassified

AD 753380

AROD-6455.6-C

FINAL REPORT

RECEIVED
DEC 1 1969

1. ARO-D proposal number: DA-31-124-AROD-466
2. Period covered by report: 7/1/66 - 6/30/69
3. Title of proposal: ELECTRONIC SPECTRA AND STRUCTURE OF LARGE MOLECULES AND CRYSTALS
4. Grant number: 6455-C
5. Name of Institution: UNIVERSITY OF PENNSYLVANIA
6. Author of report: ROBIN M. HOCHSTRASSER
7. List of manuscripts published during the grant period:
 - a. "Assignment of the Lowest Triplet State of the Carbonyl Group", S. Dym, Robin M. Hochstrasser, and Margaret Schafer, The Journal of Chemical Physics, Vol. 48, pp. 646-652, 15 January 1968.
 - b. "Spin-Orbit Coupling and Radiationless Transitions in Aromatic Ketones", S. Dym and Robin M. Hochstrasser, The Journal of Chemical Physics, Vol. 51, 6, pp. 2458-2468, 15 September 1969.
 - c. "Analytical and Structural Aspects of Vibronic Interactions in the Ultraviolet Spectra of Organic Molecules", Robin M. Hochstrasser, Accounts of Chemical Research, Vol. 1, pp. 266-274, 1968.
 - d. "Single-Crystal Spectra of Ferrimyoglobin Complexes in Polarized Light", William A. Eaton and Robin M. Hochstrasser, The Journal of Chemical Physics, Vol. 49, 3, pp. 985-995, 1 August 1968.
8. Scientific personnel supported by this project:
Robin M. Hochstrasser, Principal Investigator
Sally (Dym) Beitchman Solomon, Post Doctoral
W. A. Eaton, Ph.D. 1968
L. J. Noe, Post Doctoral

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9. Outline of Research Findings:

The first detailed study of the electronic spectrum of benzophenone crystals was completed. The triplet state at 24187 cm^{-1} was characterized as $^3\pi\pi^*$ and shown to be the analogue of the formaldehyde lowest triplet state. We showed that at least two of the spin substates are radiatively active and this work served as the stepping stone for later work on the lowest triplet states of ketones and aldehydes of aromatic molecules. Towards the end of the above grant period we published our studies of spin-orbit coupling and radiationless transitions in such molecules. We showed that the scheme describing the intersystem crossing in benzophenone was qualitatively applicable to other ketones. Spin-polarization experiments on anthrone in n-heptane at 4.2 and 2K showed that the T_z spin state was populated directly by the intersystem crossing process: In the case of anthrone we concluded that T_z was predominantly populated.

Studies of the low temperature spectra of a number of ketones showed perturbations, in the form of line broadening, that could be used to expose higher excited states of many molecules. These studies along with others done in our laboratory led us to see general principles relating line broadening to vibronic interactions between electronic states and hence to radiationless transitions. An early review of these

effects was presented in my Accounts of Chemical Research paper in which it is shown how significant information about molecular structure and non-radiative processes can be gleaned from relatively casual observations of spectral bandwidths.

The difference in linewidths for the singlet and triplet states of benzophenone was used to determine a value of ca. 10^{11} sec^{-1} for the intersystem crossing rate constant, and additional linebroadening of the vibrational bands was used to determine lower limits for vibrational relaxation times in molecular crystals.

We have shown by direct absorption spectroscopy at low temperature that aromatic ketones have low lying triplet state manifolds that consist of interlocking $n\pi^*$ and $\pi\pi^*$ states that strongly perturb one-another in the overlapping region. This work strongly suggests that the low-energy nearby states of such molecules will become an extremely fruitful area for learning more about the excited states and behavior of excited molecules. We present a mechanism for intersystem crossing in ketones that invoked direct spin-orbit coupling of vibronically modified $n\pi^*$ and $\pi\pi^*$ states through the T_z spin substate.

In other work we developed a microspectrophotometer that was used to obtain extremely precise polarized absorption spectra of derivatives of ferrimyoglobin. We showed that a PR (polarization ratio)

spectrum magnifies spectral effects that are otherwise obscured by wide absorption bands. We confirmed general features of porphyrin spectra including polarization of the B and Q states, the vibronic nature of the Q_v state, and the intensity imbalance in the Q_0 state. The PR spectrum of the azide uncovered a new electron-transfer excited state. These spectra are certainly the most accurate crystal absorption spectra yet to be obtained due to the dilute mixed crystal features of the heme-protein system and they exposed many new avenues for the investigation of the electronic structure of very large molecules.