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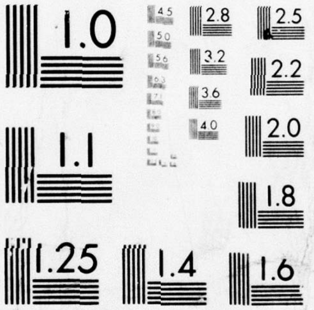
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Optical and magnetic resonance investigations of inorganic molecular solids were performed. ~~We have studied~~ optical, Raman, and zero field magnetic resonance are studied for ~~of~~ XF_6^n (X = U, Mo, W, Re, Ir) and $M(BH_4^n)_4^n$ (M = Zr, Hf, U) in order to learn about energy transfer, relaxation, and molecular solid state dynamics.

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FINAL REPORT

OPTICAL AND ZERO FIELD MAGNETIC RESONANCE SPECTROSCOPY OF INORGANIC MOLECULAR SOLIDS

U.S. Army Research Office
Grant No. DAAG29-75-G-0161
Completed 31 May 1977

Elliot R. Bernstein
Department of Chemistry
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July 1977

Statement of Problem Studied

Optical and magnetic resonance investigations of inorganic molecular solids were performed. We have studied optical, Raman, and zero field magnetic resonance of XF_6 (X = U, Mo, W, Re, Ir) and $M(BH_4)_4$ (M = Zr, Hf, U) in order to learn about energy transfer, relaxation, and molecular solid state dynamics.

Scientific Personnel Supported and Degrees Awarded

John D. Webb	Graduate Student	Ph.D., Sept. 1977
Gerald R. Meredith	Graduate Student	Ph.D., Sept. 1977
Daniel Michalopoulos	Graduate Student	
Lawrence Dennis	Postdoctoral Fellow	

Summary of Important Results

1. Interactions of inorganic molecular crystals. Electronic spectra of ReF_6 pure and mixed crystals. E. R. Bernstein and G. R. Meredith.

   Electronic absorption spectra of ReF_6 $(5d^1)$ are obtained for the pure crystal and UF_6, MoF_6, and WF_6 mixed crystals. The observed transition arises from an intraconfigurational $t_{2g} \rightarrow t_{2g}$ promotion characterized $\Gamma_{7g} \leftarrow \Gamma_{8g}$ in O_h symmetry. The pure crystal is predicted to undergo a magnetic phase transition below ~1.5 K. Pair spectra, two-molecule transitions, the ground state Jahn-Teller effect, linewidths, and vibrational assignments are discussed. The major mechanism for pair coupling and magnetic ordering is identified as superexchange through low lying delocalized charge transfer bands. These interactions are qualitatively discussed and energy localizing and delocalizing interactions are separated.

2. On the Jahn-Teller Effect in IrF_6: The Γ_{8g} $(t_{2g})^3$ State at 6800Å.
E. R. Bernstein and J.D. Webb.

In this work we present a detailed discussion of the highest energy d-d transitions of IrF_6, $\Gamma_{8g}(^2T_{2g}) \leftarrow \Gamma_{8g}(^4A_{2g})$ at 14,900 cm^{-1} and $\Gamma_{7g}(^2T_{2g}) \leftarrow \Gamma_{8g}(^4A_{2g})$ at 12,100 cm^{-1}, as observed in dilute mixed crystals with UF_6, MoF_6, and WF_6 at 4.2 and 1.8 K. The system is of particular interest because Γ_{8g} states are Jahn-Teller active and the Γ_{7g} state serves as an excellent example of what may be expected for a similar but non-Jahn-Teller active state. It is found that the usual linear Jahn-Teller interaction involving either $\nu_2(e_g)$ or $\nu_5(t_{2g})$ cannot account for the observations of both shifts and splittings of $\nu_5(\Gamma_{8g})$. In order to explain all the relevant observations, theories encompassing higher order vibronic coupling terms and/or coupled ν_2-ν_5 linear effects must be considered. Based on calculations, IrF_6 is assigned an approximate D_{4h} *symmetry in the mixed crystals. A new electronic charge* transfer state (Γ_{7g} or Γ_{6g}) is located at ~15,900 cm^{-1} and stretching vibration n (ν_1', ν_2', ν_3') (n = 1, 2) are identified built on this origin.

3. Vibrational Spectra of Transition Metal Hexafluoride Crystals. I. Orthorhombic MoF_6, WF_6, and UF_6 Neat Crystals. E. R. Bernstein and G. R. Meredith.

Neat crystal Raman spectra of orthorhombic MoF_6, WF_6, and UF_6 are presented and discussed. This work lays the foundation for presentation of two-particle and total band structures in the two following papers. The neat crystal spectra are interpreted in terms of an internal-external mode separation and a conventional factor group analysis. In general, these data lead to four essential conclusions concerning hexafluoride crystals: a) Fermi resonance plays an important role in producing the observed energy and intensity differences in this series; b) $\underline{k} = 0$

2. (continued)

exciton structures are remarkably similar in the three crystals; c) similarities and differences between these solids can be directly correlated with molecular parameters such as dipole derivatives, polarizabilities, etc.; and d) phonons (external modes) can be neatly separated into rotational and translational normal modes.

3. Vibrational Spectra of Transition Metal Hexafluoride Crystals. II. Two-Particle and Mixed Crystal Spectra as Techniques for Determination of Densities of States. E. R. Bernstein and G. R. Meredith.

In part II of this series two techniques for obtaining densities of exciton states are discussed: heavily doped mixed crystals and two-particle overtone and combination bands. It is demonstrated through Raman spectra and calculations that ($\nu_i + \nu_1$) combination bands yield very nearly true density of states functions for ν_i in the case for which ν_1 is essentially dispersionless. The mixed crystal method for density of states determinations is compared to the combination band technique and approximate mixed crystal concentrations appropriate for such studies can be calibrated for individual bands. It is pointed out that the overtone method, whenever applicable, is both simpler and more accurate for exciton state studies. Detailed analyses of ν_1 and $2\nu_1$ show that the major contribution to overtone intensity comes from the second order polarizability derivative and not anharmonic contributions.

4. Vibrational Spectra of Transition Metal Hexafluoride Crystals. III. Exciton Band Structures of MoF_6, WF_6 and UF_6. E. R. Bernstein and G. R. Meredith.

In this final paper in the series we present the overall vibrational band structure of MF_6 crystals based on the previously discussed two-particle, heavily doped mixed crystal, and neat crystal data in addition

4. (continued)

to dilute mixed crystal studies. Calculations of ν_2 and ν_5 bands based on a quadrupole-quadrupole intermolecular interaction model are determined to be in substantial agreement with the observations. The ν_1 bands are discussed in detail for a series of concentration studies and it is possible to demonstrate that MoF_6 and WF_6 conform to the ideal mixed crystal model whereas crystals containing UF_6 do not. A consistent picture of gas-to-crystal shifts, resonance interactions, band shapes and structures, densities of exciton states, Fermi resonance, and simple multipolar interaction models emerges from these studies.

5. On the Jahn-Teller Effect in ReF_6. G. R. Meredith, J. D. Webb and E. R. Bernstein.

New experimental and theoretical work has led to a re-evaluation of the Jahn-Teller effect in ReF_6. Low temperature neat and mixed crystal Raman and absorption spectra have been taken. The theory applicable to two Jahn-Teller active vibrations and to a Jahn-Teller molecule in a low symmetry crystalline field is discussed. The main conclusions of the study are that: 1) the standard linear Jahn-Teller treatment of vibronically active modes as independent motions characterized by a given vibronic angular momentum is in general inadequate; 2) Renner-Teller (quadratic) or higher order vibronic coupling terms are important; 3) crystal field splitting of the vibronic levels is not observed; and 4) vibrational exciton band widths of the Jahn-Teller active vibrations are substantially reduced.

6. Raman Spectra of SiF_4 and GeF_4 Crystals. E.R. Bernstein and G. R. Meredith.

The Raman scattering spectra of large single crystals of SiF_4 and GeF_4 at 77 K are reported. These data have been reinterpreted based on the absence of any observable changes in the spectra for scattering angles between 0° and 90°. The previous assignment of the dipole allowed ν_3 and ν_4 modes based on a TO/LO splitting model is thereby shown to be incorrect. In the absence of an apparently correct crystal structure, an exact interpretation of the data in terms of a factor group-exciton analysis is not possible; nonetheless all observations appear to be consistent with a centrosymmetric space group having a multimolecular primitive unit cell. Mixed SiF_4/GeF_4 crystal spectra have also been obtained which demonstrate that GeF_4 does not substitute into the SiF_4 lattice but that SiF_4 does enter the GeF_4 crystal substitutionally.

7. Charge-Transfer Interactions Between Transition Metal Hexafluorides and Xenon. J. D. Webb and E. R. Bernstein.

Charge-transfer interactions are reported for MF_6 (M = W, Mo, U, Re, Ir) with Xe. The nature of the charge transfer complexes is discussed. Based on spectroscopic data new estimates of MF_6 electron affinities are presented.

List of Publications

E. R. Bernstein and G. R. Meredith, Interactions of Inorganic Molecular Crystals. Electronic Spectra of ReF_6 Pure and Mixed Crystals, J. Chem. Phys. 64, 375 (1976).

E. R. Bernstein and J. D. Webb, On the Jahn-Teller Effect in IrF_6:The $\Gamma_{8g}(t_{2g})^3$ State at 6800Å, Mol. Phys. ________

E. R. Bernstein and G. R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. I. Orthorhombic MoF_6, WF_6, and UF_6 Neat Crystals. J. Chem. Phys.

List of Publications (Continued)

E. R. Bernstein and G. R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. II. Two-Particle and Mixed Crystal Spectra as Techniques for Determination of Densities of States. J. Chem. Phys.

E. R. Bernstein and G. R. Meredith, Vibrational Spectra of Transition Metal Hexafluoride Crystals. III. Exciton Band Structures of MoF_6, WF_6 and UF_6. J. Chem. Phys.

E. R. Bernstein, G. R. Meredith and J. D. Webb, On the Jahn-Teller Effect in ReF_6. Mol. Phys.

E. R. Bernstein and G. R. Meredith, Raman Spectra of Crystalline SiF_4 and GeF_4. J. Chem. Phys.

J. D. Webb and E. R. Bernstein, Charge-Transfer Interactions Between Transition Metal Hexafluorides and Xenon. J. Amer. Chem. Soc.

E. R. Bernstein, G. R. Meredith and J. D. Webb, Emission Spectra of UF_6 in Pure and Mixed Crystals. J. Chem. Phys.

E. R. Bernstein and J. D. Webb, Raman Spectra of IrF_6 Crystals Above and Below the Antiferromagnetic Phase Transition. J. Chem. Phys.

E. R. Bernstein and J. D. Webb, On Higher Order Contributions to the Linear Jahn-Teller Interactions in Transition Metal Hexafluorides. Mol. Phys.