two protons to a Be^{--} ion to form BeH_2; the nuclear repulsion term is dominant and a linear molecule is formed (similarly BH_3 will be trigonal and CH_4 tetrahedral because these arrangements minimize the nuclear repulsion energy for any given internuclear separation). However, O^{--} has ten electrons confined to a rather smaller volume than the six electrons in Be^{--} (O is smaller than Be and we have assumed that this is also true for the corresponding negative ions). Thus the two protons encounter a much greater electron density in the region of the equilibrium internuclear separation causing the net attraction term to dominate, thereby reducing the $H-O-H$ angle from 180° to 104° where the attractive force tending to superimpose the two nuclei balances the nuclear repulsion.

Thus for case (1) molecules (M belonging to the left-hand side of the periodic table) we have a common explanation of the bond angles which occur, but for case (2) molecules (i.e., M on the right-hand side of the periodic table), we have to consider each one separately. The reason for the phenomenon of directed valence is conceptually much simpler than hitherto realized, but the hope of being able to calculate explicitly any case (2) bond angles becomes far more remote. One could formalize these arguments in terms of a suitable charge density function situated on the M^{--} ion and $1s$ functions on the protons by ignoring the electronic kinetic energy. However, the kinetic energy does not remain constant during the molecule-forming process envisaged and such formalization is not therefore of much value. However, some generalizations, supported by experimental observation, about case (2) can be made: the greater the electron density around the central atom, the smaller will be the bond angle (compare the successive reduction in bond angle along the series NH_3, PH_3, AsH_3, SbH_3); also an atom in a low valence state may be case (2), but in a higher valence state may pass over into case (1) because of the increasing number of nuclear repulsions (e.g., H_2S is angular but in SF_6 the fluorine atoms take up a symmetrical arrangement of minimum nuclear repulsion). Also, $SeCl_4$ is case (1) whereas lower down the table $TeCl_4$ is a case (2) molecule in accordance with the previous generalization (compare also the series SF_6-UF_6).

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Polarization of Anthracene Crystal Fluorescence

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THE absorption spectrum of crystalline anthracene has aroused considerable attention recently in view of the current theory of molecular crystal spectra.[1] The 3800 A system has been investigated by Craig and Hobbins[2] and the reason for the departure from the "oriented gas" polarization ratio interpreted by Craig[3] as due to crystal induced mixing with the higher $^1B_{3u}$ molecular state. More recently Bree and Lyons[4] have examined the polarization properties of this system and their results have substantiated the theory developed by Craig.

Although the absorption spectrum has been thoroughly investigated the fluorescence spectrum has received little attention. Obreimov, Prikhotjko, and Shabaldas,[5] Pesteil and Barbaron,[6] and Sidman[7] have photographed the spectrum from single crystals at temperatures varying from 4°K to 20°K. However, no attempt has been made to measure the polarization properties of this fluorescence with the exception of the work of Ganguly and Choudhuri[8] which will be mentioned later. As the polarization ratio of fluorescence is an important quantity we have made a careful investigation of the fluorescence excited from anthracene crystals and also anthracene crystals containing small amounts of tetracene at room

temperature, −68°C and −196°C. We find that for single anthracene crystals (sublimation flakes) the polarization ratio (b/a) is higher than in absorption at room temperature and is about 5:1. In extending these measurements to −196°C we find no change in this ratio, however there is a shift of the spectrum to long wavelengths. In order to determine whether this shift was induced by changes in the dimensions of the unit cell at low temperatures, measurements were made on single crystals containing traces of tetracene. The tetracene fluorescence spectrum was however unchanged in position between room and low temperatures, so the shift of the anthracene fluorescence spectrum is to be correlated with the appearance of very weak absorption in the 4000 A region reported by previous workers. Although Sidman reports depolarization of the fluorescence of a number of solid solutions at low temperatures (mainly 20°K) we failed to detect any such depolarization of the tetracene fluorescence which maintains its high room temperature value of between 4 and 5 to 1 (b/a). If such a depolarization is present it must occur at lower temperatures than 77°K, and our measurements are being extended to this region.

The high value of the polarization ratio compared to the absorption value could possibly be interpreted as evidence that the fluorescence arises mainly from those regions of the crystal where the lattice symmetry is disturbed, i.e., around dislocations. It is to be expected that for such regions crystal induced mixing of the $^1B_{2u}$ with the $^1B_{3u}$ state will be weakened with a resultant return to $^1B_{2u}$ character and the "oriented gas" value (7:1). This is consistent with the exciton treatment of the crystal levels.

In order to reconcile our results with those of Ganguly and Chaudhuri $(b/a$, 1.54:1), examination of the photograph reproduced in their paper shows that the crystals they used were so thick that the first two peaks of the fluorescence spectrum are not present and, evidently the peak that they observed (the third) also suffered from reabsorption $(b>a)$ which explains the low value they report.

All of the measurements were made using a Beckman DU spectrophotometer to disperse the fluorescence which was detected by a 1P-28 photomultiplier. The fluorescence was excited by a BTU high pressure mercury lamp and a Wollaston prism was used to analyze the spectrum, only one beam being allowed to enter the spectrometer. For room temperature determinations the crystal was rotated through 90° while for low temperatures the Wollaston was rotated through 180°C.

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Raman Spectra of Phosphorous Trifluoride-Borane and Phosphorous Trifluoride-Borane-d₃†

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ALTHOUGH borane, BH_3, is not capable of existence in the free state, it is well known in compounds in which it acts as a Lewis acid. Recently, the preparation of the compound PF_3BH_3 has been reported[1] and in view of the fact that in it PF_3 exhibits an unexpected coordinating ability, it was felt there would be sufficient interest to justify a preliminary account of its Raman spectrum.

The reference to the preparation and properties of the normal and deuterated compounds has been cited; the samples after fractionation on the vacuum line were condensed into capillary Raman tubes which were then sealed off and maintained at liquid nitrogen temperatures until use. Details of the experimental

TABLE I. Observed Raman frequencies and assignments for liquid PF₃BH₃ and PF₃BD₃ at −80°C.

Frequency in cm⁻¹		Intensity and polariza- tion	Symmetry		Assignment
PF₃BH₃	PF₃BD₃				
197	169	m, dp	e	ν₁₂	PF₃ rock
370	362	vw	e	ν₁₁	F−P−F deformation
441	421	m, p	a₁	ν₅	F−P−F deformation
607	572	s, p	a₁	ν₄	P−B stretch
697±2	⋯	vw	e	ν₁₀	BH₃ rock
799		vw			diborane?
886±5	⋯	vw, p?	A₁	2ν₅	2×441 =882
920	⋯	w, p	A₁+A₂+E	ν₈−ν₁₂	1117−197 =920
944	944±5	m, p?	a₁	ν₃	P−F stretch
957±3	958±2	m, dp	e	ν₉	P−F stretch
1040±3	⋯	w, p	A₁	ν₄+ν₅	441+607 =1048
1077	⋯	w, p	a₁	ν₂	H−B−H deformation
1117	807	s, dp	e	ν₃	H−B−H deformation
⋯	1756	w	A₁+A₂+E	ν₈+ν₉	807+958 =1765
⋯	1797	vvw	E	ν₂+ν₉?	842+958 =1800
⋯	1980	vvw			diborane-d₆?
2112	⋯	vvw			diborane?
2140±4	1672±2	vw	A₁	2ν₂	2×1077 =2154
2247±2	1602	vw	A₁	2ν₈	2×1117 =2234
2328±4	⋯	vvw		2ν₃+ν₅?	calc 2329
2385	1717	vs, p	a₁	ν₁	B−H stretch
2455	1845	vs, dp	e	ν₇	B−H stretch
⋯	2431	w			B−H stretch (H impurity)
2530	⋯	vvw			diborane?
2655±5	⋯	vvw	A₁+A₂+E	ν₇+ν₁₂	197+2455 =2652

equipment have been given previously.[2] The spectra were obtained of the liquid at −80°C, qualitative polarization measurements being made on the hydrogen compound only, using the two exposure method and polaroid cylinders. The data reported in Table I represent the averages from several spectra, the estimated probable error being approximately 1 cm⁻¹ except where indicated.

Reference has been made previously[1] to the chemical similarity between PF₃ and carbon monoxide, and to the similarity in properties between phosphorous trifluoride-borane and carbon monoxide-borane. In view of the known structure of BH₃CO,[3] it would therefore be expected that the phosphorous complex would have an ethane type configuration with C_{3v} symmetry. The vibrational frequencies of such a structure are twelve in number and can be thought of in terms of the four vibrational frequencies of each of the two halves, considered as free molecules with C_{3v} symmetry, plus four vibrations arising as a consequence of the bond between the apex atoms of the two pyramids. Since free BH₃ is not known, reference can be made to the Raman frequencies of BH₃CO which have been determined recently.[4] In the B−H stretching region, two strong bands appear in the spectrum of PF₃BH₃ at 2385 and 2455 cm⁻¹ which appear to be a_1 and e type modes, respectively. Corresponding frequencies are found at 2380 and 2434 cm⁻¹ in the spectrum of liquid BH₃CO. Boron-hydrogen deformation bands are observed at 1077 and 1117 cm⁻¹ for the a_1 and e modes which again do not differ greatly from the corresponding bands at 1073 and 1101 cm⁻¹ in the carbon monoxide complex.

The frequencies associated with the PF₃ group likewise show a close similarity in pattern to those found in the Raman spectrum of liquid PF₃, which was also obtained in the present work. In this case, the a_1 and e P−F stretching frequencies at 832 and 874 cm⁻¹ shift to 994 and 958 cm⁻¹, respectively, in the complex while the a_1 and e bending frequencies shift from 484 and 351 to 441 and 370 cm⁻¹, respectively.

The remaining modes may be described as a P−B stretch, BH₃ and PF₃ rocking motions, and the inactive torsional mode. The first was easily identified as the strong polarized band at 607 cm⁻¹, while the low depolarized band at 197 cm⁻¹ is certainly the PF₃ rock. The BH₃ rock was assigned to the rather weak band at 697 cm⁻¹. No information as to the torsional frequency was obtained.

Two fundamentals of PF₃BD₃ were not observed directly. The position of the first, the symmetrical B−D bend, was estimated at 842 cm⁻¹ from its first overtone, and the position of the second, the BD₃ rock, was estimated at 603 cm⁻¹ from the comparison with

BD₃CO.[4] The calculated product rule ratios using these estimated values are 1.98 and 2.53 for the a_1 and e classes which may be compared with the theoretical values of 1.97 and 2.55. The spectra of both molecules thus are interpreted satisfactorily in terms of the C_{3v} structure.

A normal coordinate treatment is in progress and its results together with a more detailed discussion of the assignments will be published on its completion.

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Butadiene Rydberg Spectrum

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THE far ultraviolet spectrum of butadiene has been investigated by W. C. Price and A. D. Walsh.[1] It was found to consist of two Rydberg Patterns converging to a common limit. In this letter we wish to present a theoretical discussion of the butadiene Rydberg spectrum.

In the approximation of the semiempirical molecular orbital theory, butadiene is characterized by the ground states (1) $cis(^1A_1)$ $−(\psi_{b_2})^2(\psi_{a_2})^2$ and (2) $trans(^1A_g)−(\psi_{a_u})^2(\psi_{b_g})^2$. These give rise to the Rydberg transitions (1) $cis−\psi_{a_2}→np$, nd, etc., and (2) $trans−\psi_{b_g}→np$, nf, etc. Now if for simplicity in calculating the term values we assume that butadiene has a linear carbon skeleton, we find that the hydrogenic energy levels split as follows: np becomes a doublet $(np_x,np_{y,z})$, nd a triplet, nf a quartet, and so forth. The additional splitting of the hydrogenic energy levels produced by the nonlinearity of the butadiene carbon skeleton is small.[2] Thus, since only two pronounced Rydberg patterns have been found,[1] we may identify the butadiene Rydberg transition as $\psi_{b_g}(trans)→np(trans)+\psi_{a_2}(cis)→np(cis)$. This assignment predicts a multiplet-like structure for the butadiene Rydberg series.[3]

The theoretical considerations given above for butadiene hold equally well for isoprene and the alkyl substituted butadienes. Hence, we would expect their spectra to be similar to that of butadiene. This similarity has been observed.[1]

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² The calculation of Rydberg term values for polyatomic molecules is described in A. D. Liehr, Z. Naturforsch (to be published).
³ The small splitting of the nearly degenerate np_y and np_z Rydberg levels, and the excitation of torsional vibrations in the np Rydberg state should also give a complex appearance to the two observed Rydberg progressions. This complexity has been noted by Price and Walsh.¹

On the Nuclear Physical Stability of the Uranium Minerals

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AN attempt is made in this paper to apply the nuclear reactor theory in geochronology and to explain certain interrelations between the age and the nuclear physical stability of the uranium minerals, as well as the geological environments of the mineral formation.

The infinite multiplication constant, k_∞, may be considered as an indicator of the stability of the uranium minerals, which are the natural assemblages of uranium, moderator, and impurities. We