

TABLE I. Observed Raman frequencies and assignments for liquid PF<sub>3</sub>BH<sub>3</sub> and PF<sub>3</sub>BD<sub>3</sub> at -80°C.

Frequency in cm <sup>-1</sup>		Intensity and polarization	Symmetry	Assignment
PF <sub>3</sub> BH <sub>3</sub>	PF <sub>3</sub> BD <sub>3</sub>			
197	169	m, dp	<i>e</i>	ν <sub>12</sub> PF <sub>3</sub> rock
370	362	vw	<i>e</i>	ν <sub>11</sub> P-F deformation
441	421	m, p	<i>a</i> <sub>1</sub>	ν <sub>8</sub> P-F deformation
607	572	s, p	<i>e</i>	ν <sub>10</sub> P-B stretch
697 ± 2	...	vw	<i>e</i>	ν <sub>10</sub> BH <sub>3</sub> rock
799	...	vw		diborane?
886 ± 5	...	vw, p?	<i>A</i> <sub>1</sub>	2 × 441 = 882
920	...	w, p	<i>A</i> <sub>1</sub> + <i>A</i> <sub>2</sub> + <i>E</i>	1117 - 197 = 920
944	944 ± 5	m, p?	<i>a</i> <sub>1</sub>	ν <sub>2</sub> P-F stretch
957 ± 3	958 ± 2	m, dp	<i>e</i>	ν <sub>9</sub> P-F stretch
1040 ± 3	...	w, p	<i>A</i> <sub>1</sub>	ν <sub>4</sub> + ν <sub>6</sub> 441 + 607 = 1048
1077	...	w, p	<i>a</i> <sub>1</sub>	ν <sub>2</sub> H-B-H deformation
1117	807	s, dp	<i>e</i>	ν <sub>8</sub> H-B-H deformation
...	1756	w	<i>A</i> <sub>1</sub> + <i>A</i> <sub>2</sub> + <i>E</i>	ν <sub>8</sub> + ν <sub>9</sub> 807 + 958 = 1765
...	1797	vwv	<i>E</i>	ν <sub>2</sub> + ν <sub>9</sub> ? 842 + 958 = 1800
...	1980	vwv		diborane-d <sub>2</sub> ?
2112	...	vwv		diborane?
2140 ± 4	1672 ± 2	vw	<i>A</i> <sub>1</sub>	2 × 1077 = 2154
2247 ± 2	1602	vw	<i>A</i> <sub>1</sub>	2 × 1117 = 2234
2328 ± 4	...	vwv		calc 2329
2385	1717	vs, p	<i>a</i> <sub>1</sub>	ν <sub>1</sub> B-H stretch
2455	1845	vs, dp	<i>e</i>	ν <sub>7</sub> B-H stretch
...	2431	w		B-H stretch (H impurity)
2530	...	vwv		diborane?
2655 ± 5	...	vwv	<i>A</i> <sub>1</sub> + <i>A</i> <sub>2</sub> + <i>E</i>	ν <sub>1</sub> + ν <sub>12</sub> 197 + 2455 = 2652

equipment have been given previously.<sup>2</sup> 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<sup>-1</sup> except where indicated.

Reference has been made previously<sup>1</sup> to the chemical similarity between PF<sub>3</sub> and carbon monoxide, and to the similarity in properties between phosphorous trifluoride-borane and carbon monoxide-borane. In view of the known structure of BH<sub>3</sub>CO,<sup>3</sup> it would therefore be expected that the phosphorous complex would have an ethane type configuration with C<sub>3v</sub> 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<sub>3v</sub> symmetry, plus four vibrations arising as a consequence of the bond between the apex atoms of the two pyramids. Since free BH<sub>3</sub> is not known, reference can be made to the Raman frequencies of BH<sub>3</sub>CO which have been determined recently.<sup>4</sup> In the B-H stretching region, two strong bands appear in the spectrum of PF<sub>3</sub>BH<sub>3</sub> at 2385 and 2455 cm<sup>-1</sup> which appear to be *a*<sub>1</sub> and *e* type modes, respectively. Corresponding frequencies are found at 2380 and 2434 cm<sup>-1</sup> in the spectrum of liquid BH<sub>3</sub>CO. Boron-hydrogen deformation bands are observed at 1077 and 1117 cm<sup>-1</sup> for the *a*<sub>1</sub> and *e* modes which again do not differ greatly from the corresponding bands at 1073 and 1101 cm<sup>-1</sup> in the carbon monoxide complex.

The frequencies associated with the PF<sub>3</sub> group likewise show a close similarity in pattern to those found in the Raman spectrum of liquid PF<sub>3</sub>, which was also obtained in the present work. In this case, the *a*<sub>1</sub> and *e* P-F stretching frequencies at 832 and 874 cm<sup>-1</sup> shift to 994 and 958 cm<sup>-1</sup>, respectively, in the complex while the *a*<sub>1</sub> and *e* bending frequencies shift from 484 and 351 to 441 and 370 cm<sup>-1</sup>, respectively.

The remaining modes may be described as a P-B stretch, BH<sub>3</sub> and PF<sub>3</sub> rocking motions, and the inactive torsional mode. The first was easily identified as the strong polarized band at 607 cm<sup>-1</sup>, while the low depolarized band at 197 cm<sup>-1</sup> is certainly the PF<sub>3</sub> rock. The BH<sub>3</sub> rock was assigned to the rather weak band at 697 cm<sup>-1</sup>. No information as to the torsional frequency was obtained.

Two fundamentals of PF<sub>3</sub>BD<sub>3</sub> were not observed directly. The position of the first, the symmetrical B-D bend, was estimated at 842 cm<sup>-1</sup> from its first overtone, and the position of the second, the BD<sub>3</sub> rock, was estimated at 603 cm<sup>-1</sup> from the comparison with

BD<sub>3</sub>CO.<sup>4</sup> The calculated product rule ratios using these estimated values are 1.98 and 2.53 for the *a*<sub>1</sub> 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<sub>3v</sub> 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.

\* This research was conducted under Contract AF 23(616)-8 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

<sup>1</sup> G. L. Vidale and R. C. Taylor, J. Am. Chem. Soc. 78, 294 (1956).

<sup>2</sup> R. W. Parry and T. C. Bissot, J. Am. Chem. Soc. 78, 1524 (1956).

<sup>3</sup> Gordy, Ring, and Burg, Phys. Rev. 78, 512 (1950).

<sup>4</sup> R. C. Taylor (to be published).

## Butadiene Rydberg Spectrum

ANDREW D. LIEHR\*

Mallinckrodt Laboratory, Harvard University,  
Cambridge, Massachusetts

(Received July 30, 1956)

THE far ultraviolet spectrum of butadiene has been investigated by W. C. Price and A. D. Walsh.<sup>1</sup> 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* (<sup>1</sup>A<sub>1</sub>) - (ψ<sub>b2</sub>)<sup>2</sup>(ψ<sub>a2</sub>)<sup>2</sup> and (2) *trans* (<sup>1</sup>A<sub>g</sub>) - (ψ<sub>a1</sub>)<sup>2</sup>(ψ<sub>b1</sub>)<sup>2</sup>. These give rise to the Rydberg transitions (1) *cis* - ψ<sub>a2</sub> - n*p*, *nd*, etc., and (2) *trans* - ψ<sub>b1</sub> - n*p*, *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<sub>z</sub>, np<sub>x</sub>, n*), *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.<sup>2</sup> Thus, since only two pronounced Rydberg patterns have been found,<sup>1</sup> we may identify the butadiene Rydberg transition as ψ<sub>b1</sub> (*trans*) - n*p* (*trans*) + ψ<sub>a2</sub> (*cis*) - n*p* (*cis*). This assignment predicts a multiplet-like structure for the butadiene Rydberg series.<sup>3</sup>

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.<sup>1</sup>

\* National Science Foundation Postdoctoral Fellow, 1955-1956. Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

<sup>1</sup> W. C. Price and A. D. Walsh, Proc. Roy. Soc. (London) A174, 220 (1940).

<sup>2</sup> The calculation of Rydberg term values for polyatomic molecules is described in A. D. Liehr, Z. Naturforsch. (to be published).

<sup>3</sup> The small splitting of the nearly degenerate *np<sub>z</sub>* and *np<sub>x</sub>* 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.<sup>1</sup>

## On the Nuclear Physical Stability of the Uranium Minerals

P. K. KURODA

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas

(Received July 26, 1956)

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<sub>∞</sub>*, may be considered as an indicator of the stability of the uranium minerals, which are the natural assemblages of uranium, moderator, and impurities. We

TABLE I.  $\rho$ ,  $f$ ,  $\eta$ , and  $k_{\infty}$  of a Johanngeorgenstadt pitchblende. Chemical composition of the mineral: 1 mole  $\text{UO}_2$ ;  $\frac{1}{2}$  mole  $\text{H}_2\text{O}$ ; 0.0  $n$  moles  $\text{PbO}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{SiO}_2$ ; 0.00  $n$  moles  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ , alkalis,  $\text{SO}_3$  and  $\text{P}_2\text{O}_5$ .

Geological time (million years)	0 (present)	700	1000	1400	2100	2800
$\text{U}^{235}$ enrichment (percent)	0.7	1.3	1.6	2.3	4.0	7.0
$\rho$	0.47	0.45	0.43	0.42	0.38	0.34
$f$	0.93	0.95	0.96	0.97	0.98	0.99
$\eta$	1.32	1.57	1.66	1.77	1.91	1.98
$k_{\infty}$	0.58	0.67	0.69	0.72	0.71	0.67

may consider a system to be quite "stable," when the infinite multiplication constant of the assemblage is far less than unity. The system will be nuclear physically "unstable," when the infinite multiplication constant is greater than unity.

According to the nuclear reactor theory,

$$k_{\infty} = \epsilon p f \eta, \quad (1)$$

where  $\epsilon$  is the fast fission factor,  $p$  is the resonance escape probability,  $f$  is the thermal utilization factor, and  $\eta$  is the number of fast neutrons available per neutron absorbed by uranium.

When dealing with geological events, the change of the uranium enrichment as a function of geological time should also be taken into consideration. The major neutron sources in minerals are the spontaneous fission and the  $(\alpha, n)$  reactions.

The values of  $\rho$  and  $f$  can be calculated if the chemical composition of the mineral is given,  $\epsilon$  is always close to unity, and  $\eta$  as a function of the uranium enrichment is known.<sup>1</sup> Hence the value of  $k_{\infty}$  of a mineral at any geological time can be calculated.

Table I shows the calculated values of  $\rho$ ,  $f$ ,  $\eta$ , and  $k_{\infty}$  of a sample of Johanngeorgenstadt pitchblende.<sup>2</sup> Similar calculations show that most of the uranium minerals were nuclear physically "stable" during the past 2800 million years, provided the water content of the minerals had remained unchanged during the geological past. It is worthy of note, however, that a slight increase of the water to uranium ratio could have easily caused a sharp upward change of  $\rho$ , without affecting  $f$  considerably, and the result of which could have been enough to make the system nuclear physically "unstable."

It is generally accepted that the deposition of the uranium minerals took place at the pegmatitic-pneumatolytic and early hydrothermal stages. Hence, one may consider that the crystallization of the uranium minerals represents the following sequence of events. An aqueous solution of uranium ( $\text{U}^{235}$  enriched) is gradually converted to an assemblage of uranium plus  $n$  moles of water ( $n=1, 2, 3, \dots, n$ ) and finally to an almost water-free uranium mineral.

Let us imagine that the crystallization of the Johanngeorgenstadt pitchblende took place 2100 million years ago. The calculated values of  $\rho$ ,  $f$ ,  $\eta$ , and  $k_{\infty}$  are shown in Table II. Table II shows that the assemblages of the Johanngeorgenstadt pitchblende plus water were nuclear physically "unstable" 2100 million years ago, and the critical uranium chain reactions could have taken place, if the size of the assemblage was greater than, say, a thickness of a few feet. The effect of such an event could have been a sudden elevation of the temperature, followed by a complete destruction of the critical assemblage.

The effect of the ground water or the water vapor from the molten magma could have resulted in the formation of a nuclear physically "unstable" assemblage of uranium plus  $n$  moles of

water. Such mechanism might explain the fact that the ages of the large uranium deposits never exceed 2000 million years, or the marked discrepancies exist between the  $\text{Pb}^{206}/\text{U}^{238}$  age and the  $\text{Pb}^{207}/\text{Pb}^{206}$  age of the uranium minerals.

This investigation was made possible by support from the U. S. Atomic Energy Commission.

<sup>1</sup> The method of calculations is described in the following reference books; Samuel Glasstone, *Principles of Nuclear Reactor Engineering* (Princeton University Press, Princeton, 1955); Raymond L. Murray, *Introduction to Nuclear Engineering* (New York, 1954); Richard Stephenson, *Introduction to Nuclear Engineering* (New York, 1954).

<sup>2</sup> F. W. Clarke, *The Data of Geochemistry* (Washington, 1924).

## Determination of Electron Affinities by Extrapolation\*

S. GELTMAN

Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland

(Received August 2, 1956)

THE first, and perhaps the most straightforward type of empirical calculation used to determine atomic electron affinities,<sup>1</sup> was the quadratic extrapolation of the electron binding energy from isoelectronic systems of higher atomic number. Since then many other extrapolation procedures<sup>2</sup> have been suggested and have achieved limited success. The purpose of the present note is to describe a procedure which is essentially an extension of the original method of Glocker,<sup>1</sup> but which provides more physical insight regarding the validity of the derived affinities. The linear, quadratic, cubic, quartic, . . . extrapolations of the electron binding energy may be expressed as

$$E_0(n) = \sum_{i=1}^{n+1} (-1)^{i+1} \frac{(n+1)!}{(n-i+1)!} E_i$$

for  $n=1, 2, 3, 4, \dots$ , where  $E_i$  is the ionization energy of the atom or positive ion of atomic number  $Z+i$  isoelectronic with the negative ion  $Z$ . We thus have a set of  $E_0$ 's corresponding to values of the discrete variable  $n$ . Let us now adopt the assumption that the best value of the electron affinity is that extrapolated value corresponding to the lowest energy, that is, where  $dE_0/dn=0$ . This may be regarded as a sort of empirical variational calculation for the energy.

Table I contains four values of  $E_0$  and the best affinity obtained therefrom for all the elements in the first two rows of the periodic table.<sup>3</sup> No stable negative ions of He, Be, N, Ne, Mg, or A are expected to exist. The maximum binding energy of an electron to B lies between  $n=2$  and 3 and is so close to zero that one could not make any predictions about the existence of  $\text{B}^-$  from this table. The maxima for C and O lie between  $n=1$  and 2 and hence we can at best set a lower limit to their affinities. The quadratic extrapolation for H is in good agreement with the theoretical value<sup>4</sup> of

TABLE I. Extrapolations and best affinities.

	$n=1$	$E_0(n)$ (ev)	2	3	4	Best affinity
H	-26.459	0.733	0.708	0.706	~0.733	
He	-7.426	-0.528	-0.472	-0.427	<0	
Li	-6.509	0.377	0.392	0.373	~0.392	
Be	-7.784	-0.814	-0.762	-0.776	<0	
B	-7.077	-0.089	-0.07	-0.1	~0	
C	-6.07	0.83	0.71	0.50	>0.83	
N	-7.75	-0.6	-0.3	0.1	<0	
O	-6.23	0.70	0.57	0.22	>0.70	
F	-4.17	2.93	3.02	3.03	~3.03	
Ne	-4.75	-1.24	-1.00	-0.85	<0	
Na	-3.535	-0.08	0.12	0.3	>0.3	
Mg	-4.37	-0.91	-0.77	-0.57	<0	
Al	-3.35	0.5	1.2	1.7	>1.7	
Si	-2.3	1.4	1.6	1.4	~1.6	
P	-3.09	0.57	1.33	2.68	>2.68	
S	-1.60	2.1	3	3	>2.1	
Cl	-0.30	3.05	3.1	3.1	~3.1	
A	-3.19	-1.01	-0.82	-0.8	<0	

TABLE II. The water-uranium ratio and the values of  $\rho$ ,  $f$ ,  $\eta$ , and  $k_{\infty}$  (Johanngeorgenstadt pitchblende, 2100 million years ago).

$n$	1/4	1/2	1	2	3	4	5	10
$\rho$	0.29	0.47	0.62	0.74	0.79	0.82	0.84	0.86
$f$	0.99	0.98	0.97	0.95	0.93	0.91	0.89	0.81
$\eta$	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91
$k_{\infty}$	0.55	0.88	1.15	1.34	1.40	1.42	1.43	1.33