

neglected. The energy of the metallic lattice is then composed of the following parts:

- (1) Electrostatic energy $\sim -1/d$ (taken from Wigner and Seitz²)
- (2) Exchange energy after Bloch³ $\sim -1/d$
- (3) Correlation energy after Wigner⁴ (from Fig. 7 of ⁴)
- (4) Thomas-Fermi energy $\sim 1/d^2$
- (5) Additional energy = El. density $\times \int_r^1 \frac{1}{r} e^{-2\kappa r} d\tau = \frac{2\pi A}{k^2} \frac{1}{d^3}$.

The Table I gives the values found in this way for the heat of sublimation and d_0^* . Through improvement of the uniform distribution of the valence electron in the lattice, a further approach of the heat of sublimation to the experimental value may be attained. That the additional energy reproduces well the influence of the kernels upon the valence electron is demonstrated by the calculated $\partial^2 E / \partial V^2$ which agrees much better with the experimental data than the calculation of Rice,⁵ who instead of our introduction of the additional energy assumed the kernels to be impenetrable and determined their radius empirically from d_0 itself. The relationship between sublimation energy, ionization energy and the work function first established by Wigner and Bardeen⁶ is also valid in this theory.

TABLE I.

N/a	LATTICE CONST. (A)		BINDING ENERGY (ev)		$\partial^2 E / \partial V^2$ (E: ENERGY, V: ATOMIC VOLUME) (10^{18} erg·cm ⁻⁶)			WORK FUNCTION (ev)	
	calc.	exp.	calc.	exp. ⁵	calc.	exp. ⁵	calc. Rice ⁵	calc.	exp. ⁶
Na	4.35	4.24	0.91	1.13	1.59	1.9	4.7	1.96	2.25-2.46
K	5.20	5.25	0.85	0.94	0.47	0.53	1.33	1.95	2.17-2.24
Rb	5.75	5.62	0.594	0.865	0.24	0.17	0.89	1.90	2.16-2.19
Cs	6.15	6.05	0.599	0.83	0.15	0.065	0.58	1.86	1.81-1.96

Column 4 gives the work function calculated in this way, omitting the double layer term. When one bears in mind that the only empirical data used are the spectra of the free atoms the agreement is satisfactory and there is the hope that this simple approximation method will prove useful for further metallic problems where the more vigorous methods become involved in formal difficulties.

The complete work will appear in the *Acta Physico-chimica U.R.S.S.*

H. HELLMANN
W. KASSATOTSCHKIN

Karpow-Institute for Physical Chemistry,
Moscow,
March 15, 1936.

*Li was omitted, as in this case the application of a statistical method is not free of arbitrariness.

¹ H. Hellmann, J. Chem. Phys. **3**, 61 (1935); Acta Physicochimica U.R.S.S. **1**, 913 (1935); **4**, 225 (1936).

² E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934).

³ F. Bloch, Zeits. f. Physik **57**, 545 (1929).

⁴ E. Wigner, Phys. Rev. **46**, 1002 (1934).

⁵ O. K. Rice, J. Chem. Phys. **1**, 649 (1933).

⁶ E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935).

The Raman Spectra of Carbon and Silicon Tetrafluorides

We have photographed the Raman spectra for the tetrafluorides of carbon and silicon in both the liquid and gaseous states. The results are presented in Table I together with the Raman frequencies of CCl₄ for purposes of comparison. The relative intensities are given in parentheses.

TABLE I.

	ω_1 (cm ⁻¹)	ω_2 (cm ⁻¹)	ω_3 (cm ⁻¹)	ω_4 (cm ⁻¹)
CF ₄	904 (10)	437 (1)	(1200)	635 (1)
SiF ₄	800	(285)	(1000)	(431)
CCl ₄	450	214	775	311

So far only ω_1 for SiF₄ has been found, the other three lines being apparently of small intensity. For gaseous CF₄ only ω_1 was definitely seen on the plates, and it was sharp and strong. ω_2 and ω_4 together with ω_1 were obtained from CF₄ (1) at -120° .

The CF₄ was prepared by treating carbon (Norit) with fluorine gas and submitting the raw product to a number of fractional distillations. It is difficult to prepare pure CF₄. The SiF₄ was prepared by a conventional method.

The assignment of frequencies is based on a number of considerations. Since ω_1 is the completely symmetrical vibration, it should appear intense and sharp in the Raman spectrum. Accordingly the strongest and sharpest observed line was assigned to ω_1 . It was found, from a consideration of the Raman spectra for eight tetrahalides that certain regularities existed (approximate constancy of ratios of corresponding frequencies), and on the assumption that no discontinuities in these regularities would occur with CF₄ the frequencies ω_2 and ω_4 were assigned.

The frequencies given in parentheses were computed from empirically found ratios, or from the formulae derived from normal coordinate treatments of tetrahedral molecules by Urey and Bradley,¹ and Rosenthal.²

Two absorption bands in the infrared spectrum of CF₄ have been observed recently by Eucken and Bertram,³ namely, $\omega_3 = 1350$ cm⁻¹ and $\omega_4 = 653$ cm⁻¹. The latter is in fair agreement with 635 cm⁻¹ found in the Raman spectrum, and the estimate (1200) for ω_3 is, considering the theory involved, in accord with $\omega_3 = 1350$ cm⁻¹. Eucken and Bertram estimate ω_2 to be 503 cm⁻¹ from specific heat measurements, and this agrees only moderately well with the observed value, $\omega_2 = 437$ cm⁻¹. The disagreement is probably to be assigned to errors in the theory or measurement of the specific heats.

DON M. YOST
EDWIN N. LASSETRE
SIEGFRIED T. GROSS

California Institute of Technology,
Pasadena, California,
April 6, 1936.

¹ Urey and Bradley, Phys. Rev. **38**, 1970 (1932).

² Rosenthal, Phys. Rev. **45**, 538 (1931).

³ Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).