

Metallic Binding According to the Combined Approximation Procedure

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does not preclude the possibility that they may be extant, but if so they are very much weaker than the same shifts in the dehydrated acid." It is principally with this remark that Angus and Leckie disagree, as they state: "... the Raman spectra obtained from the saturated aqueous solutions of oxalic acid and from the dihydrated oxalic acid crystals are substantially the same." However, they add: "Our results, obtained from crystals which were definitely dihydrate crystals, agree with those of Rao . . ." and, "Since Hibben's conclusions that the two carboxyl groups behave differently depend to a large extent on the difference in the spectra of the anhydrous and hydrated crystals we submit that such conclusions may be invalidated by his comparing the spectrum he obtained for his anhydrous crystals with Rao's spectrum for the solid."

The last quotation leaves such an erroneous impression that it is necessary to correct it. As pointed out in the first paragraph of this note, the different behavior of the two carboxyl groups is predicated on the observed magnitudes of the two carbonyl shifts and not on a comparison of the anhydrous, or hydrated material with the solution, consequently these conclusions are not affected by the presence or absence of such shifts in the hydrated material.

The apparent weakening of these lines in the anhydrous acid and their greater weakening (or absence) in the hydrated compound were explained by this writer as possibly attributable to chelation. If Angus and Leckie's observations are correct this explanation would be without significance. Nevertheless Rao's results cannot be cited in entire support of themselves since his published photographs show clearly that in the hydrate or anhydrous acid (it is immaterial to the argument which he used) the relative intensities of the carbonyl frequencies are markedly reduced as compared with the solution, in contradistinction to the first statement of Angus and Leckie's previously quoted. The intensities published by Rao are: (for $\Delta\tilde{\nu}$ 1640 and 1740, respectively) crystal: 00, 1; solution: 1, 3; or approximately a 66 percent decrease taking $\Delta\tilde{\nu}$ 845 as a reference standard. It is unfortunate that in republishing Rao's data Angus and Leckie omitted the intensities, which indicate an agreement with the present writer.

The fact that carbonyl shifts may weaken is already well known from the spectra of acid salts. So far as the hydrate is concerned Zachariasen⁴ from x-ray measurements has concluded that the C—O bond in this compound is at least part of the time a single bond, and that this substance is not a normal hydrate of oxalic acid.

It is believed that some of the difficulties of interpretation may have arisen in the use of an unfiltered mercury spectrum as a source of excitation. The O—H band, unusually sharp, falls in approximately the same position as the C=O shifts and the 4730 Hg line overlaps in the same position.

JAMES H. HIBBEN

Geophysical Laboratory,
Carnegie Institution of Washington,
January 21, 1936.

¹ Angus and Leckie, *J. Chem. Phys.* **4**, 83 (1936).

² Hibben, *J. Chem. Phys.* **3**, 675 (1935).

³ S. Rao, *Zeits. f. Physik* **94**, 536 (1935).

⁴ Zachariasen, *Phys. Rev.* **45**, 755 (1934).

Reply to Dr. Hibben's Letter

Dr. Hibben's criticisms may be answered very briefly. His suggestion that our results for the dihydrate crystals are vitiated by incomplete filtration of the 4047A Hg line is incorrect since we used a strong solution of NaNO₂ as a filter and the 4047 undisplaced Hg lines were very weak on the plates. His second quotation from our letter tends to misrepresent the arguments put forward by us. We must maintain our view that Rao's crystals, showing frequencies at approximately 1660 and 1760 cm⁻¹, were dihydrate crystals and that Rao's results, therefore, support our own observations. We have satisfied ourselves that our results are correct.

The purpose of our letter was merely to indicate differences in results which, as we pointed out, *may* invalidate some of Hibben's conclusions. We do not think that the point at issue is sufficiently important to merit an extended controversy.

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ALAN H. LECKIE

University College,
London, W.C.1.,
February 19, 1936.

Metallic Binding According to the Combined Approximation Procedure

A combined approximation procedure has been proposed by one of us¹ for the calculation of the chemical interaction between atoms. In this method the atomic kernel is treated according to Thomas-Fermi and the valence electron by a Schrödinger equation. The total action of the kernel upon the valence electron—inclusive of the Pauli principle—then goes over into an additional potential in the Schrödinger equation, which can be taken approximately from the spectra. The application to K₂ and KH gave plausible results, however, on account of the omission of higher approximations they were still not absolutely convincing. We have therefore applied the combined approximation procedure to the problem of metallic binding. Here one can easily take into account the interactions between the valence electrons to a higher degree of approximation than in single molecules.

It was established in the beginning that the law $-1/r + (A/r)e^{-2\kappa r}$ for the total field of the kernel gives a good approximation in the case of the free Mg atom: When A and κ were so determined that the lowest s term and p term of Mg⁺ were rendered correctly, then Ritz's method (with r_{12} in the eigenfunction) yielded good results for the ground term of Mg. For the alkali metals A and κ were determined from the two lowest s terms with the aid of one-parameter hydrogen-like eigenfunctions. Since the field of the ion determined in this way runs a rather flat course, it is sufficient in the first approximation to set the valence electron in the lattice equal to a plane wave. The interaction of the kernels arising from their overlapping is

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 $\times \int_0^1 \frac{1}{r} e^{-2\pi r} d\tau = \frac{2\pi A}{k^2} \frac{1}{d^3}$.

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. (Å)		BINDING ENERGY (ev)		$\partial^2 E / \partial V^2$ (E : EN- ERGY, V : ATOM- IC VOLUME) (10 ²⁸ 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.*

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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.

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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).