

Erratum : Heats of Combustion and Formation of Some Organosilicon Compounds

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The accuracy of the calculated figures is regarded as satisfactory since the basic molecular parameters and vibrational frequencies do not involve any major uncertainties. The only frequency which has not yet been located precisely is the non-planar bending frequency ω_8 of species a'' , for which Herzberg and Reid's¹ value of 670 cm^{-1} has been accepted in the present calculations.

The assignment of some overtone bands is less certain, and the problem of inversion doubling, especially in the bending frequency ω_3 , has not been looked into so far. By a method outlined earlier,³ the inversion barrier in HNCO is estimated to be as low as $V_{\pi} = 5.6\text{ kcal/mole}$, i.e., of the same order of magnitude as in NH_3 . Judging from the experience⁴ with NH_3 , however, it may be concluded that below 1500°K such inversion doubling would not affect the thermodynamic functions significantly.

¹ G. Herzberg and C. Reid, *Disc. Faraday Soc.* **9**, 92 (1950).

² W. J. O. Thomas, *Trans. Faraday Soc.* **49**, 855 (1953).

³ N. W. Luft, *Disc. Faraday Soc.* **14**, 114 (1953).

⁴ K. S. Pitzer, *J. Chem. Phys.* **7**, 251 (1939).

BaTiO₃-KF Phase Diagram

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IT has been found that on the BaTiO_3 rich side of the eutectic composition, the liquidus temperatures¹ obtained by the differential thermal analysis techniques are low. This was also pointed out to the author by workers at Bell Telephone Laboratories.² Depression of the liquidus, it is believed, was introduced by supersaturation which was apparently relatively constant throughout the various determinations, hence escaping early detection.

Work is being continued on this system and it is hoped that a complete phase equilibrium diagram, for the KF-rich end at least, will be obtained. As an interim measure, more nearly correct liquidus temperatures have been determined by straightforward solubility measurements. Solubility data appear in Table I.

TABLE I. Mole percent solubility of BaTiO_3 in KF vs temperature.

Temp., °C	1000	1050	1100	1150	1200	1250	1300
BaTiO_3 , mole %	4	6	9	12½	17	22½	28½

¹ C. Karan and B. J. Skinner, *J. Chem. Phys.* **21**, 2225 (1953).

² Private communication from S. O. Morgan, based on unpublished work of S. S. Flaschen.

Erratum: Heats of Combustion and Formation of Some Organosilicon Compounds

[*J. Chem. Phys.* **19**, 1330 (1951).]

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IN Table I of the paper referred to above, $-\Delta H_R$ and $-\Delta H_f^0$ are to be amended as shown in Table I. In this table we adopted the value $-208\text{ kcal mole}^{-1}$ instead of the older value used in our previous paper for the heat of formation of silica.

TABLE I. Molar heat of combustion and formation at 20°C .

Substance	$-\Delta H_R$ kcal mole^{-1}	$-\Delta H_f^0$, kcal mole^{-1} obs
Hexamethylcyclotrisiloxane	1407	396
Hexaphenylcyclotrisiloxane	4810	225
Diethylsilanediol	782	212
Dimethyldiethoxysilane	1119	200
Di- <i>n</i> -propyldiethoxysilane	1751	217

Polar Solvent Effects on the Absorption Spectra of Metallic Complexes

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ABSORPTION spectra of metallic complexes generally have two absorption bands, the first lies in the visible region, and the second in the near ultraviolet. Adjacent to these bands, many complexes show strong absorptions usually designated as the specific band. One of the authors, Tsuchida, has previously discussed their origins in terms of electronic structure. According to Tsuchida,¹ the first band is due to d or f electrons in an unsaturated shell of the central metallic ion, the second band is attributed to coordination electrons, and the specific band is caused by the ligand itself.

After study of quantitative correlation between the first and the second bands, Soné² has concluded that both bands should be ascribed to the same origin. Inamura and Kondo³ studied the absorption spectra of Ir^{III} and Ir^{IV} complexes and suggested that both bands may be due to the coordination electrons. However, the optical rotatory dispersion of d $[\text{Co en}_3]\text{Br}_3$ ⁴ shows that the contribution of each band to the rotatory power is remarkably different. Moreover, the dichroism of Co-praseo salt⁵ in the case that the bands have inverted dichroic properties. As stated above,

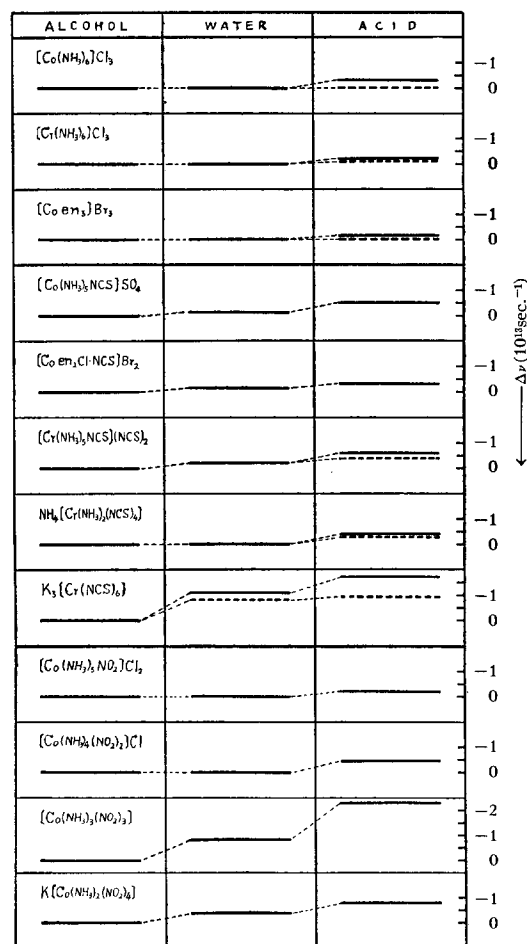


FIG. 1. The solvent behavior of the first and the second bands: —, first band; ---, second band. (In the case of nitro and some rhodanato complexes, overlapping of the second band by the strong specific band prevents measurement of the second band maximum.)

the origins of the absorption bands in metallic complexes have been a subject of much discussion and conflicting evidence.

The present work was undertaken to investigate the relation between the type of bands and their behavior in a series of polar solvents. Measurements of absorption spectra of typical metallic complexes in alcoholic solution, water, and acetic acid solution were made using a Beckman Model DU spectrophotometer. In order to compare the magnitude of the relative shift, the maxima of the first and the second bands in an alcoholic solution are shown on the same level in Fig. 1. The figure shows definitely that both bands become progressively more bathochromic as the solvent is changed in the order, alcohol, water, and acetic acid (red shift). The only difference between them is that the first band is generally shifted more markedly than the second band.

The solvent behavior of the specific band is, however, in the opposite direction to the first and the second bands as is shown in Fig. 2. That is, the band becomes progressively more hypsochromic in the same order of the solvents (blue shift). Irregularity is found in rhodanato complexes, but it may be due to some special interaction between the rhodanato group and acetic acid.

If we compare our results with that of McConnell,⁶ we find that the first and the second bands correspond to the $\pi-\pi$ absorption, whereas the specific band corresponds to the $n-\pi$ absorption. In fact, absorption spectra of amine and ethylenediamine complexes which have bound lone pair electrons for coordination do not show the specific bands, while the complexes which have CN^- , NO_2^- , ONO^- , H_2O , NCS^- , SO_4^{2-} , NO_3^- , OH^- , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , Cl^- ,

CrO_4^{2-} , Br^- , I^- , etc., as ligands always indicate their own specific bands. This fact suggests that the specific absorption originates in the lone pair electrons of the ligands. In regard to the first and the second bands, however, a conclusion cannot be drawn at the present time as to whether both of them should be ascribed to the same type of electrons or not. Experimental work is now in progress which may lead to a better theoretical explanation.

- ¹ R. Tsuchida, Bull. Chem. Soc. Japan **13**, 388, 436, and 471 (1938).
² K. Soné, J. Chem. Soc. Japan **71**, 270, 316, and 364 (1950).
³ Y. Inamura and S. Kondo, J. Chem. Soc. Japan **72**, 787 and 840 (1951).
⁴ M. Kobayashi, J. Chem. Soc. Japan **72**, 787 and 840 (1950).
⁵ S. Yamada and R. Tsuchida, Bull. Chem. Soc. Japan **25**, 127 (1952).
⁶ H. McConnell, J. Chem. Phys. **20**, 700 (1952).

Nuclear Quadrupole Resonance in Ethyl Chloroformate and Ethyl Trichloroacetate*

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 (Received March 18, 1954)

PURE quadrupole resonance has been observed in ethyl chloroformate and ethyl trichloroacetate at liquid nitrogen temperature. Observations were made using a simple regenerative oscillator, Zeeman modulation, and a phase-sensitive detector. Frequencies were measured with a Signal Corps BC-221 frequency meter calibrated against radio station WWV. The Cl^{35} resonance frequencies are listed in Table I along with the resonance frequencies for trichloroacetyl chloride reported by Allen.¹

TABLE I

1. Ethyl chloroformate	$\text{Cl}-\text{C}-\text{O}-\text{C}_2\text{H}_5$ O	33.858
2. Trichloroacetyl chloride ^a	$\text{Cl}-\text{C}-\text{CCl}_3$ O	33.721 40.132 40.473 40.613
3. Ethyl trichloroacetate	$\text{C}_2\text{H}_5-\text{O}-\text{C}-\text{CCl}_3$ O	40.200 40.339

* Data from reference 1.

Comparison of the structural formulas and resonance frequencies for these molecules illustrates the effect of chemical bonding on nuclear quadrupole resonance pointed out by Livingston² and Allen.³ In molecules 1 and 2 the chlorine atoms on the left end have almost identical bonding to the carbon atom and their resonance frequencies are almost the same. In molecules 2 and 3 the CCl_3 groups have almost identical bonding to the molecule, and again the resonance frequencies for the chlorine atoms are about the same.

The existence of two resonances for the CCl_3 group of ethyl trichloroacetate and three for the same group in trichloroacetyl chloride is probably a result of the difference in crystal structure of the two molecules.

- * Sponsored by the Office of Ordnance Research, U. S. Army.
¹ H. C. Allen, J. Am. Chem. Soc. **74**, 6074 (1952).
² Ralph Livingston, J. Phys. Chem. **57**, 496 (1953).
³ H. C. Allen, J. Phys. Chem. **57**, 501 (1953).

Erratum: Author Index to Volume 21

[J. Chem. Phys. **21**, 2249 (1953)]

THE first line after the name of "Clark, Joan R." should read:

Cleveland, Forrest F. (see Bernstein, Richard B.)—1778, 1903(L).

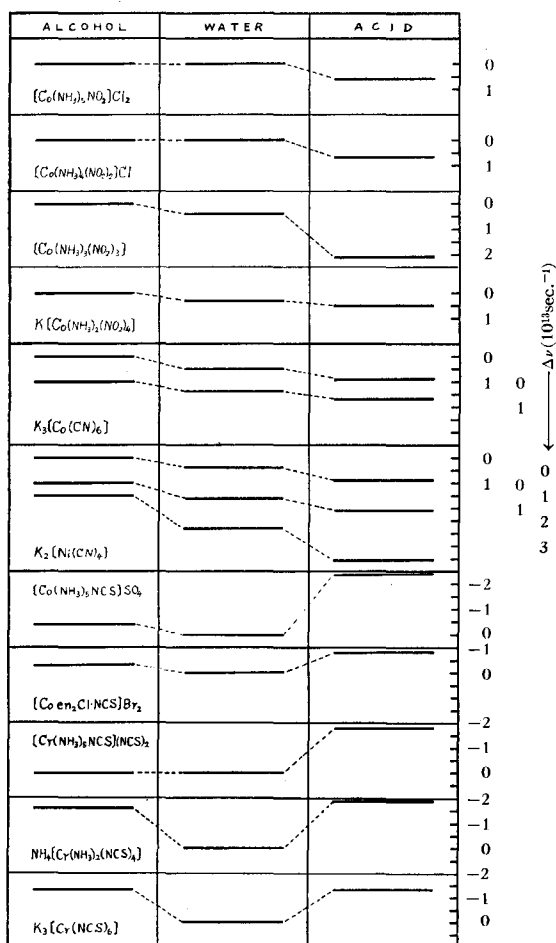


FIG. 2. The solvent behavior of the specific band. (Cyan complexes indicate two or three peaks.)