

On the Assignment of the TripletSinglet Emission of Benzene

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The electronic spectrum of chlorine monofluoride has been investigated by Wahrhaftig⁵ and Schmitz and Schumacher.⁶ From a value for ω_e and $X_{e\omega_e}$ given by these authors, the fundamental is predicted to fall at 773.4 cm⁻¹ and at 772.4 cm⁻¹, respectively. Both are in good agreement with the observed position.

The first overtone falls in a region of strong water vapor absorption at 6.26 μ , which has hampered the study of the band. Using a 10-cm cell filled to a pressure of $\frac{1}{3}$ atmos., a band centered at 1535 cm⁻¹ has been observed. This is 8 cm⁻¹ higher than the position predicted from the electronic spectrum, but is probably within the experimental error introduced by water vapor absorption.

Figure 2 shows a microphotometer tracing of the Raman spectrum of liquid ClF. A single line is observed at a shift of 758 cm⁻¹. This is to be compared to the value 772 cm⁻¹ for the fundamental of the gas. Attempts to resolve the line to show the isotope effect have been unsuccessful.

* This document is based on work performed for the AEC by Carbide and Carbon Chemicals Corporation, at Oak Ridge, Tennessee.

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⁶ See reference 1, p. 359.

Note on the Derivation of the Frequency Spectrum of a Crystal from Specific Heat Measurements

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THE portion of the specific heat of a solid which is due to lattice vibrations is given by

$$C_v(T) = 3R \int_0^\infty E(h\nu/kT) \rho(\nu) d\nu, \quad (1)$$

where $E(x) = x^2 e^x / (e^x - 1)^2$ and $\rho(\nu) d\nu$ is the number of modes of vibration in the frequency range ν to $\nu + d\nu$. Equation (1) has usually been used to calculate $C_v(T)$ on the basis of a more or less reasonable assumption concerning the frequency spectrum $\rho(\nu)$. It would be of great interest to calculate $\rho(\nu)$ from experimental values of $C_v(T)$. Montroll¹ has given a method by which this problem can be formally solved, but the solution involves gamma- and zeta-functions of a complex argument, which have not yet been tabulated, with laborious numerical integration.

One of us (J.P.S.) has devised a much less laborious method. Let $pkT/h = \tau$, $p\nu = t$, $C_v(T) = \gamma(\tau)$, $\rho(\nu) = g(t)$, where p is an arbitrary constant. Let also $E(x)$ be expanded in powers of e^x . Equation (1) becomes

$$\tau^2 \gamma(\tau) = (3R/p) \sum_{n=1}^\infty n \int_0^\infty t^2 g(t) e^{-n t / \tau} dt. \quad (2)$$

Let

$$t^2 g(t) = (2p/\pi) \sum_{m=1}^\infty a_m (1 - \cos mt) / m, \quad (3)$$

which is chosen because the Laplace transform has a convenient form. We then obtain

$$\gamma(\tau) = 3R \sum_{m=1}^\infty a_m (\coth m\pi\tau - 1/m\pi\tau). \quad (4)$$

In order that $\gamma(\tau)$ may represent the specific heat of a solid, it must satisfy the following asymptotic conditions. For large values of τ , $\gamma(\tau) \rightarrow 3R$, therefore $\sum a_m = 1$. As $\tau \rightarrow 0$ the specific heat approaches zero as $A\tau^3$, where A is an experimental constant.

Therefore $\sum m a_m = 0$ and $\sum m^3 a_m = (15A/R)(h/\pi p k)^3$. The arbitrary constant p is chosen so as to make the important values of τ lie within a tractable range. Then it is possible, using at most six terms of the series, to make the function (4) agree very well with any specific heat which is due only to lattice vibrations, and which therefore increases monotonously. Finally the frequency spectrum can be determined by means of Eq. (3).

An attempt has been made to apply this method to bismuth, which has no transitions below 300°K and has a negligible electronic specific heat,² but which evidently has a vibration spectrum very different from that of an elastic continuum. The experimental curve was constructed from measurements by Keesom and van den Ende³ below 12°K, Armstrong and Grayson-Smith⁴ from 14° to 22°K, and Anderson⁵ above 60°K. These were combined by plotting a smooth curve of the apparent Debye Θ as a function of T .

There was no difficulty in fitting the smoothed curve of C_v with a function of the form (4), and hence of deriving a function $\rho(\nu)$. The derived frequency spectrum showed a steep double maximum at frequencies which dominate in determining the specific heat around 50°K, where two sets of data join. However, the result proved to be extremely sensitive to details of the specific heat curve in the region where dC_v/dT is large. A slight change in the manner of smoothing the data made the two maxima coalesce into a single, much less marked maximum. This disappointing result is clearly intrinsic to the problem, and is not due to using only a finite number of terms, because $\rho(\nu)$ is unique for a given fitted curve $\gamma(\tau)$. Montroll's method must therefore give the same result for the same smoothed curves, with the same sensitivity to a small change in the smoothing.

The conclusion is that the mathematical problem of inverting Eq. (1) can be solved with a reasonable amount of labor, but that no physical meaning can be attached to the result unless the original experimental data have a higher degree of internal consistency than any at present available. To obtain any information on crystal vibrations in this way it will be necessary to have accurate specific heat measurements, made on the same sample by the same method, throughout the range 2° to 300°K. We have been unable to find a single suitable example.

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On the Assignment of the Triplet-Singlet Emission of Benzene

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CALCULATIONS have been made upon the triplet states of benzene in a non-empirical approximation¹ taking account of configuration interaction² between configurations based on molecular orbital wave functions. The results agree with the valence-bond theory³ and the single-configuration molecular orbital theory⁴ in making the $^3B_{1u}$ state the lowest of the triplets, lower than the $^3B_{2u}$ state by 2.5 ev in this calculation. There is thus an unusual measure of agreement between the theoretical methods on the identity of this lowest triplet state, comparable only with the agreement there is between them that the lowest singlet state is $^1A_{1g}$.

However, Shull's observation⁵ that active origins in the triplet-singlet emission of benzene are provided by b_{2g} as well as e_{2g} vibrations has been interpreted by Shull, and by McClure,⁶ to mean that the triplet state concerned (presumably the lowest triplet state) has some $^1B_{1u}$ character; and further, using selection rules analogous to those for intercombinations in diatomic molecules, McClure⁶ has deduced from this that the triplet state must

be ${}^3B_{2u}$ and not ${}^3B_{1u}$ as favored theoretically. The purpose of this note is to suggest that active b_{2g} vibrations may occur also in a ${}^3B_{1u}-{}^1A_{1g}$ transition and therefore that the experimental facts at present available are not against the identification of the lowest triplet state as ${}^3B_{1u}$.

It is a question of the mixing by combined magnetic (spin-orbit) and vibrational perturbations of the triplet state with either the well-known ${}^1E_{1u}$ state (for perpendicular bands) or with an A_{2u} state (parallel bands). Since the magnetic perturbations act on space wave functions as A_{2g} or E_{1g} operators⁶ there are the following possibilities.

(i) If the triplet state is ${}^3B_{1u}$, the total space perturbation required is E_{2g} for perpendicular bands and B_{2g} for parallel bands. The relevant decompositions into spin-orbit and vibrational perturbations are:

$$E_{2g} = A_{2g} \times e_{2g}; \quad E_{1g} \times b_{2g}; \quad E_{1g} \times e_{1g}.$$

$$B_{2g} = A_{2g} \times b_{1g}; \quad E_{1g} \times e_{2g}.$$

The first symbol applies to the magnetic and the second to the vibrational perturbation. There are of course no actual b_{1g} vibrations of benzene.

(ii) If the triplet state is ${}^3B_{2u}$, perpendicular bands demand a total space perturbation E_{2g} , and parallel bands B_{1g} . The decompositions for the first have already been given. For the second they are: $B_{1g} = A_{2g} \times b_{2g}; \quad E_{1g} \times e_{2g}$.

These decompositions, which exhaust the possibilities, show that active b_{2g} vibrations may be accounted for in cases (i) and (ii), and in neither case is it necessary to assume borrowing from parallel-type transitions, whose existence in benzene is as yet uncertain. It is however necessary to invoke the in-plane component of the spin-orbit coupling which cannot cause mixing of pure π -type electronic wave functions but acts only in cooperation with vibrations. This latter fact might account for the weakness of the b_{2g} perturbations relative to e_{2g} , and the whole situation would then run parallel with a case studied by Garforth and Ingold⁶ in the fluorescence of benzene, in which case both perturbations are vibrational: Garforth and Ingold showed that two out-of-plane vibrations, b_{2g} and e_{1g} , neither of which separately is capable of mixing π -type electronic wave functions, can together effect considerable mixing of the plane symmetric ${}^1B_{2u}$ and ${}^1E_{1u}$ states of benzene.

The writer concludes therefore that the designation ${}^3B_{1u}$ for the lowest triplet state of benzene remains tenable.

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Magnetic Susceptibilities of $TiCl_2$ and Tl_2Cl_3

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THALLIUM chlorides corresponding to the empirical formulas $TiCl_2$ and Tl_2Cl_3 have been known for many years. Although the empirical formulas may appear to indicate valence states of thallium other than the well-known +1 and +3, the configuration, first proposed by Werner,¹ which represents these compounds as thallos chlorothallates is usually assumed.^{2,3} In this manner, $TiCl_2$ has been considered to represent $Tl^I/Tl^{III}Cl_2$, and Tl_2Cl_3 to represent $Tl^I_2/Tl^{III}Cl_3$. The evidence⁴ for this representation is that these chlorides resemble other chlorothallates of the types $CuTiCl_4$ and $(NH_4)_3TiCl_6$. Also, recently McConnell and Davidson⁵ have shown by the use of radioactive thallium that the thallium atoms in Tl_2Cl_3 are not equivalent, which is the expected result if the compound is a thallos chlorothallate. Still, it has not been conclusively demonstrated that valence states other than +1 and +3 are not present in either $TiCl_2$ or Tl_2Cl_3 . We

have investigated this question by measurements of the magnetic susceptibilities of the two solid compounds.

The ground state electronic configuration of gaseous thallium atoms is $6s^26p$ beyond the gold core.⁶ Both $Tl(I)$ and $Tl(III)$ would thus be expected to be diamagnetic, and this has been shown for $Tl(I)$ by Klemm and Tilk.⁷ A +2 state would be paramagnetic because of one unpaired electron, provided this state does not exist as a dimer, analogous to Hg_2^{++} , for which diamagnetism would be expected. This appears to be the situation for the dichlorides of gallium and indium, the congeners of thallium. The dichlorides of these two elements are diamagnetic.⁷ Since neither element possesses a stable +1 oxidation state, it is unlikely that these compounds would be represented in the same manner as $TiCl_2$ above. It is more likely that these +2 ions are dimers.⁸

$TiCl_2$ and Tl_2Cl_3 were prepared according to directions given by Mellor.⁴ $TiCl_2$ was prepared by passing a slow stream of anhydrous Cl_2 over anhydrous $TiCl$. The reaction tube was heated sufficiently to maintain the reaction mixture in a molten condition, and the Cl_2 was passed over the mixture until no further change in appearance of the molten mixture could be detected. A color change of dark brown to pale yellow was noted as the reaction progressed. After solidification the compound was very pale yellow in color. Since this compound is not stable in the presence of water, all subsequent transfer operations were carried out in a dry box. Tl_2Cl_3 was prepared by saturating a boiling solution of $TiCl_3$, slightly acidified with nitric acid, with freshly precipitated $TiCl$. Upon allowing the solution to cool, bright yellow crystals of Tl_2Cl_3 separated. These were washed repeatedly with small portions of hot water to dissolve any of the more soluble $TiCl$ that might have coprecipitated. The product was dried in an oven at 105°C.

Weighed amounts of the compounds were analyzed by reducing the thallium to the +1 state with SO_2 , precipitating and weighing the thallium as Tl_2CrO_4 , and precipitating and weighing the chloride as $AgCl$. The analytical results are as follows: $TiCl_2$, 73.8 percent Tl , 26.6 percent Cl (calculated: 74.24 percent Tl , 25.76 percent Cl); Tl_2Cl_3 , 79.2 percent Tl , 20.8 percent Cl (calculated: 79.35 percent Tl , 20.65 percent Cl).

The magnetic susceptibilities of the solids were measured at room temperature by the Gouy method.⁹ For each determination the weight of sample taken was approximately 5 grams.

Both $TiCl_2$ and Tl_2Cl_3 were found to be diamagnetic. This indicates, as discussed above, that these compounds are either thallos chlorothallates, with only +1 and +3 thallium, or if +2 thallium is present it exists as a dimer.

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The Dissociation Energies of the C—H Bond in Propylene and the C—C Bond in Butene-1

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IT was expected that the recent investigation of the pyrolysis of propylene¹ would provide the necessary data for the estimation of the C—H bond dissociation energy in this compound; this then, in conjunction with relevant thermochemical data, would make it possible to compute the heat of formation of allyl radical. The experimental results—supplemented by a further study of