

lines are shifted toward lower energies. Later runs revealed even greater shifts, as much as 19 kev for the 46.9 kev line. Line positions were always closely reproducible when thin aluminum backing was used.

Source thicknesses for the beta-spectrum were estimated to be less than 0.1 mg/cm². Nylon windows 0.08 mg/cm² were used to close the argon-ethylene filled counter used as detector. No correction was made for window absorption.

The author is indebted to Professor J. S. Foster, Director of this Laboratory, for his keen interest in this work, and to Mr. J. S. Fraser for many valuable discussions and for assistance in taking spectrometer data.

* Obtained from Johnson Matthey, London, England.

¹ G. T. Seaborg and I. Perlman, *Rev. Mod. Phys.* **20**, 585 (1948).

² C. H. Braden *et al.*, *Phys. Rev.* **74**, 1539 (1948).

Anomalies in the Microwave Spectrum of Methyl Cyanide and Methyl Iso-Cyanide

HARALD H. NIELSEN

*Mendenhall Laboratory of Physics, The Ohio State University,
Columbus, Ohio*

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THE microwave spectra of methyl cyanide and methyl isocyanide have been studied by Gordy¹ who has observed three lines in the former case and four lines in the latter case which can be shown to originate with rotational transitions in an excited vibration state. The electric moment lies along the axis of symmetry so that $\Delta K = 0$. From the general positions of the lines in the spectrum Gordy has identified them with transitions $J = 1 \rightarrow J = 2$.

The lines observed by Gordy occur at the frequencies 36870.94 mc, 36903.40 mc and 36942.15 mc in the spectrum of methyl cyanide and at 40313.37 mc, 40364.07 mc, 40366.55 mc and 40424.49 mc in the spectrum of methyl iso-cyanide. The general pattern in the former case consists of two lines separated by a frequency interval of about 72 mc with a third line almost in the center of these. In the latter example the two extreme lines are separated by an interval of about 111 mc with two lines near the center of these separated by an interval of 1.5 mc. These patterns cannot be explained on the basis of a rigid symmetric rotator, but require that certain degeneracies be removed.

It seems reasonable to suppose that the excited vibration states which here are involved are the frequencies ω_s in the two molecules, namely 380 cm⁻¹ and 290 cm⁻¹. These are doubly degenerated perpendicular vibrations and associated with each of them there exists one unit of internal angular momentum of vibration. A Coriolis interaction between vibration and rotation splits the levels where $K \neq 0$ into two components, the separation between components being $Kh/2\pi^2 I_{zz} c$. Examination of the Hamiltonian for a symmetric molecule reveals that the component state corresponding to the situation where the molecular framework remains at rest (i.e., $K = l$) may further be split by an l -type doubling.²

The magnitude of the l -type doubling may be calculated accurately only when the normal coordinate problem has been solved and the shape of the molecule is known. An estimate may nevertheless be made which may be regarded as a fair approximation. Taking B to be 0.335 cm⁻¹ and $\omega_s = 290$ cm⁻¹ for methyl cyanide these splittings may be estimated to be about 0.0047 cm⁻¹ and 0.0015 cm⁻¹ respectively for the states $J = 1$ and $J = 2$. The appropriate selection rule yields a pattern like the one observed with the two extreme lines separated by about 0.0031 cm⁻¹ (93 mc) and two lines near the center separated by a much smaller interval of the order of 3×10^{-5} cm⁻¹ (1.0 mc). For methyl cyanide the splittings for $J = 1$ and $J = 2$ are respectively predicted to be 0.003 cm⁻¹ and 0.001 cm⁻¹ and the line pattern will be similar to the

former, the extreme lines in the pattern being here separated by about 0.002 cm⁻¹ (i.e. 60 mc) with two lines near the center, their separation being about 1.3×10^{-5} cm⁻¹ (i.e. 0.4 mc). Since the two central lines would have the same frequency except for centrifugal distortion it is proposed that the single line observed by Gordy in the latter case is in reality two unresolved lines. Because of the roughness of the approximation the agreement with experiment is regarded as satisfactory. A further check is the comparison of the interval between the extreme lines in the two cases. Experimentally this ratio is about 0.65 and the theory indicates a ratio of 0.64.

The theory of l -type doubling in polyatomic molecules will be discussed in detail later with specific applications to the above two molecules.

The author wishes to express his gratefulness to Professor Walter Gordy for having made his measurements available to him.

¹ Walter Gordy, private communication.

² It is found that in the original work of Nielsen and Shaffer (*J. Chem. Phys.* **11**, 140 (1943)) an error in sign was introduced. Two terms of equal magnitude which were cancelled against each other should have been added together. When this correction is made the coefficient of the matrix element in the case of a linear molecule becomes $(Be^2/2\omega_s) [1 + 4\sum_s \xi_{ss} \lambda_s / (\lambda_s - \lambda_s)]$, where $\lambda_s = 4\pi^2 c^2 \omega_s^2$, instead of $(Be^2/2\omega_s)$. This change appears to bring the theoretical relations for l -type splitting in linear molecules into substantial agreement with experiment.

Polarization of the Vacuum

JERZY RAYSKI*

N. Copernicus University, Torun, Poland

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THE problem of the vacuum polarization and the closely connected question of the photon self-energy has recently caused much confusion. As is well known, Heisenberg¹ obtained for the photon self-energy a logarithmic divergence while Wentzel² found a finite but non-zero value. On the other hand Schwinger³ believes that there is no doubt in the gauge invariance of the formalism and demonstrates that the photon self-energy is strictly zero.

The reason for this discrepancy is as follows: The proofs of the gauge invariance are based on the assumption that the Schrödinger equation possesses a solution. But in frames of the quantized field theory (at least in case of two coupled fields), this assumption is obviously not true. The quantized field equations possess no solution and, after the unitary transformations, the gauge invariance must be restored again (similarly to the mass and charge constants which must be restored by renormalization).

The basic expressions for the vacuum polarization containing products of $\bar{\Delta}$ and $\Delta^{(1)}$ functions and their derivatives are mathematically meaningless at the light cone⁴ so that by formal operations on non-existing integrals one may obtain any result one likes. The most straightforward evaluation yields for the photon self-energy a quadratically divergent result. Heisenberg obtained a logarithmic divergence only because he arbitrarily subtracted a part of the effect.

In order to give a mathematical meaning to such expressions as e.g. products of $\bar{\Delta}$ and $\Delta^{(1)}$ functions on the light cone a special regularizing procedure is needed. This may be achieved by replacing $\Delta \Delta^{(1)}$ by a (finite) sum

$$\bar{\Delta}(m_0) \cdot \Delta^{(1)}(m_0) \rightarrow \sum_i C_i \bar{\Delta}(m_i) \Delta^{(1)}(m_0).$$

m_0 is the mass of the electron while m_i , $i = 1, 2, \dots$ play only an auxiliary role and are assumed to tend to infinity. C_i are constants ($C_0 = 1$) such that

$$\sum C_i = 0, \quad \sum C_i m_i^2 = 0. \quad (I)$$

The above mentioned procedure secures the consistency of the calculations but, on the other hand, means a departure from the wave equation. It cannot be considered as a theory but rather as a provisional remedy.⁴

Another possibility, which seems promising, is to combine several charged fields with different transformation character of their field functions.⁵ The photon self-energy due to the interaction with electrons is negative while the same quantity due to the interaction with charged scalar particles is positive. Both are quadratically divergent so that a compensation is possible. The conditions for compensation show a remarkable analogy with the conditions (I) for regularization and may be considered as conditions for the existence of a solution of the Schrödinger equation.

* Present address: Eidg. Techn. Hochschule, Zürich.

¹ W. Heisenberg, *Zeits. f. Physik* **90**, 209 (1934).

² G. Wentzel, *Phys. Rev.* **74**, 1070 (1948).

³ J. Schwinger, *Phys. Rev.* **75**, 651 (1949).

⁴ An extensive report on invariant regularization, criticism of relativistic electrodynamics, etc. is in preparation by W. Pauli and F. Villars. To appear probably in *Rev. Mod. Phys.* The present author is indebted to both authors for the opportunity of seeing their paper before publication.

⁵ J. Rayski, *Acta Phys. Polonica* **IX**, 129 (1948).

Paramagnetic Resonance Spectra of Five Chromic Sulfate Alums

B. BLEANEY*

Clarendon Laboratory, Oxford, England

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THE anomalous behavior at low temperatures of the paramagnetic resonance spectra of ammonium and potassium chromic alums previously reported¹ has been further investigated by measurements at small intervals of wave-length between 3 cm and 10 cm. In addition, rubidium, cesium and methylamine chromic alums have been studied for comparison. The spectra of these five alums at low temperatures show fundamental differences in character, corresponding to the following groupings:

Group 1. Rubidium, cesium and methylamine chromic alums.

—These alums exhibit the "normal" chromic alum spectrum at all temperatures down to 20°K. By "normal spectrum" is meant that associated with a predominantly cubic crystalline electric field on which is superimposed a small trigonal component with symmetry about the (111) axis. The presence of such a field was originally deduced by Van Vleck,² and the room temperature spectra of all the chromic alums so far studied³⁻⁶ conform to this type. The splittings between the two doublets of the spin quadruplet deduced from this spectrum at various temperatures are listed in Table I. As the

pendence is probably associated with thermal contraction, which becomes zero at low temperatures. No further change in the splitting is anticipated below 20°K; the small discrepancy between the value given for the cesium alum and that of 0.138 ± 0.002 cm⁻¹ obtained by Benzie and Cooke⁷ from paramagnetic relaxation measurements at 1°K may be due to a contribution from spin-spin interaction to the specific heat greater than that calculated from pure dipolar interaction.

Group 2. Ammonium chromic alum.—No further measurements have been made on the "normal" spectrum observed at high temperatures, but analysis of the unresolved line at 90°K indicates a splitting just above the transition point of about 0.03_5 cm⁻¹. Below the transition point the spectrum is quite different, and it was previously assumed, in virtue of Kramers' theorem, that the splitting of 0.314 cm⁻¹ measured by plotting the transitions back into zero magnetic field was the only one present. Continuation of this plotting to longer wave-lengths has revealed, however, the presence of a second splitting equal to 0.242 ± 0.003 cm⁻¹. It seems necessary to ascribe these two splittings to different ions in the unit cell which must, therefore, be substantially different in structure from the high temperature modification. The splittings are in substantial agreement with the average value of 0.27 ± 0.01 cm⁻¹ of Benzie and Cooke,⁷ if the two types of ion are present in roughly equal proportions, as is suggested by the relative intensities of the absorption peaks in the paramagnetic resonance spectrum.

Group 3. Potassium chromic alum.—The splitting deduced from the high temperature spectrum falls to a minimum value of about 0.03_5 cm⁻¹ at 160°K. There is no sudden transition at this temperature, however, but as the temperature is lowered side peaks in the spectrum appear whose intensity increases steadily down to 20°K without marked change in position. This process is reversible without observable hysteresis if the temperature is increased again. As with the ammonium salt two splittings are observed, but they are much more different in magnitude (see Table I). The resemblance^{1,5} to the normal spectrum with a splitting of ca. 0.17 cm⁻¹ (which would agree well with measurements by other methods⁸⁻¹⁰) is thus only superficial, and the relative intensities of the various peaks are not of the right order of magnitude.

No satisfactory explanation of this behavior of the potassium salt has been propounded which can be reconciled with the following facts: (a) The specific heat of the spin system, as determined from paramagnetic relaxation measurements,⁸ is the same at 90°K as at helium temperatures, and considerably lower than calculated from the two splittings unless a much smaller fraction of the ions have the higher splitting than have the lower value. This latter is not suggested by the relative intensities in the paramagnetic spectrum. The intensities are all abnormally low, however, and it may be that a proportion of the ions have yet another splitting too small to observe. On the other hand, no such distribution of splittings could account for the plateau in the entropy curve at 0.05°K found by de Klerk, Steenland and Gorter¹¹ falling below $R \log_e 2$, which seems to require that the Kramers degeneracy be partly lifted.

Van Vleck² has shown that the splitting in the chromic alums is due partly to the direct field of the more distant atoms and partly to the distortion of the local octahedron of water molecules. The distortion required (0.03 A.U.) is so small that it may well change sufficiently with temperature as the crystal contracts to account for the temperature dependent part of the splitting. The contribution from the more distant atoms should be substantially independent of temperature, and is estimated by Van Vleck as about 0.05 cm⁻¹. It may be significant that the minimum splitting in both the ammonium and potassium alums is 0.03_5 cm⁻¹, and that this represents the effect of the more distant atoms.

TABLE I. Splittings (cm⁻¹) in various chromic alums at low temperatures.

| Temperature | Ammonium | Potassium | Rubidium | Cesium | Methylamine |
|-------------|------------------------------|------------------------------|--------------|--------------|--------------|
| 290°K* | 0.135 | 0.12 | 0.165 | 0.145 | 0.165 |
| 193°K | 0.085 | 0.055 | 0.126 | 0.134 | |
| 90°K | 0.035 | 0.26 (0.15 ± .01) | 0.108 ± .002 | 0.133 ± .002 | 0.170 ± .003 |
| | transition point | | | | |
| 80°K | 0.314 ± .003 0.242 ± .003 | | | | |
| 20°K | 0.317 ± .003 0.240 ± .003 | 0.270 ± .003 (0.15 ± .01) | 0.108 ± .002 | 0.133 ± .002 | 0.170 ± .003 |

* Values at 290°K are from unpublished work of Bagguley and Griffiths (see reference 6). Probable error where not given is ± 0.005 cm⁻¹.

alum is cooled from room temperature, the splitting decreases somewhat (except in the case of the largest monovalent ion CH₃NH₃) but becomes constant below 90°K. Since the splitting is sensitive to very small distortions of the octahedron of water molecules around the Cr⁺⁺⁺ ion, its temperature de-