Zero-THz Polarisation Band of Metal Acetylacetonates

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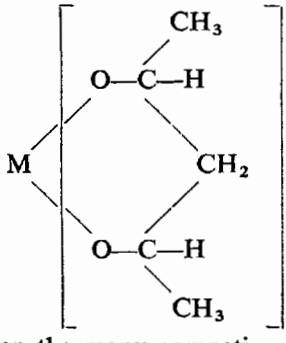
Received 10*th November*, 1978

The "anomalous polarisation" of certain metal acetyl acetonates is evaluated between radio and submillimetre frequencies for the series $Be(AcAc)_2$, $Al(AcAc)_3$, $Fe(AcAc)_3$, $Cr(AcAc)_3$ and $Zr(AcAc)_4$ in benzene solution. The compounds exhibit a loss peak at ≈ 8 mm, whose cross-section is small for the beryllium compound and increases in the above sequence. The total polarisation may thus be conveniently divided into this part and a virtually constant portion spanning the frequency region from 4 to $\approx 200\ cm^{-1}$. The "anomalous" polarisation may thus be described adequately in conventional terms.

The high frequency absorption of metal acetyl acetonate compounds has been the subject of renewed interest since the advent of Fourier spectroscopy, which has permitted the study of the far infrared portion of the so-called "anomalous" absorption in these species. Haigh *et al.*[1] and Angel [2] have recently detailed the nature of the problem and discussed the implications of measurements over the complete millimetre/submillimetre range of frequencies (up to terahertz frequencies).

The purpose of this article is to remove existing ambiguities and settle the factual positions concerning $P_{total}:P_{dipole}:P_{atomic}$. We report results for the following series of compounds: $Be(AcAc)_2$ (tetrahedral); $Al(AcAc)_3$, $Fe(AcAc)_3$ and $Cr(AcAc)_3$ (all octahedral); $Zr(AcAc)_4$ (cubic) in the frequency range of interest. Here AcAc stands for the ligand ring:



To distinguish between the many competing theories advanced in the literature demands a high precision in the experimental results. Hence, the measurements presented here have been carefully and systematically checked so that uncertainties over the whole frequency range are 2 % or less. For these metal complexes in benzene solution the total high frequency "atomic polarisation" is comprised of

two contributions. A microwave component [virtually absent in $Be(AcAc)_2$], and an almost constant far infrared component. This approximate constancy is observed despite the different numbers of the ligand rings present in the different metal chelates and scans the frequency range from ≈ 4 to 200 cm^{-1}.

EXPERIMENTAL

MICROWAVE

A travelling wave transmission method was used for dielectric loss measurements at 8.41 and 4.33 mm. A detailed discussion of the apparatus and experimental procedure is given elsewhere.[3] The method enables the attenuation per unit length of a dielectric sample to be measured by varying the sample depth.

FAR INFRARED

A Grubb–Parsons/N.P.L. Mark III Michelson type interferometer incorporating phase modulation was used for far infrared measurements. The signal was detected with a diamond-windowed Golay pneumatic cell. Reproducibility of the spectra is estimated as ± 2 % over 90 % of the frequency range of study.

Samples were prepared and recrystallized by standard techniques. The benzene solvent was of " analytical grade ", carefully dried over molecular sieves. All results were recorded at ambient temperature, 293 K.

RESULTS AND DISCUSSION

Data are presented in fig. 1 and 2 as absorption coefficient (in neper cm^{-1} dm^3 mol^{-1}) plotted against cm^{-1}. These are corrected for solvent absorption using:

$$\frac{(A_\phi)_{soln}}{(A_\phi)_{pure}} = \frac{(M_\phi)^2_{soln} + (M_x M_\phi)_{soln}}{(M_\phi)^2_{pure}}$$

where A denotes absorption; M molarity; ϕ benzene and x the solute. On the graph of ε'' against $\ln \nu$ (fig. 3, one example shown) extrapolation by hand is required for ease of integration. This procedure is necessary generally because of the paucity of microwave data. For the Al and Cr acetyl acetonates a value of ε'' is available at 2.2 mm; the ε'' values for $Be(AcAc)_2$ approach this so that a loss value of ε''/X_2 of ≈ 0.17 at 2.2 mm appears to be a common feature for these substances in benzene solvent. This value (adjusted for concentration) has been used for the iron and zirconium compounds (where no measurement is available at 2.2 mm) and a straight line drawn from it to the value at 20 cm^{-1} in the far infrared.

The tetrahedral $Be(AcAc)_2$ exhibits almost no loss (or polarization) in the microwave; the octahedral Al, Fe and Cr compounds are intermediate, and the cubic $Zr(AcAc)_4$ exhibits a much larger microwave loss. The polarizations are calculated by integration of the ε'' against $\ln \bar{\nu}$ curves. The results of this integration are shown in table 1, reproducible to about ± 1 cm^3, the main uncertainty [4] arising from the extrapolation from 4 to 20 cm^{-1}.

If roughly 10 % of the radio-frequency–visible polarisation difference ($P_{RF} - P_{vis}$) can be attributed to absorption at wave numbers greater than 200 cm^{-1} then the remainder is composed of a microwave component [small for $Be(AcAc)_2$] and an almost constant value of 25 ± 3 cm^3 for the far infrared component, suggesting strongly that the latter's origin is an intramolecular mode of the ligand AcAc, not unduly affected by the central metal ion.

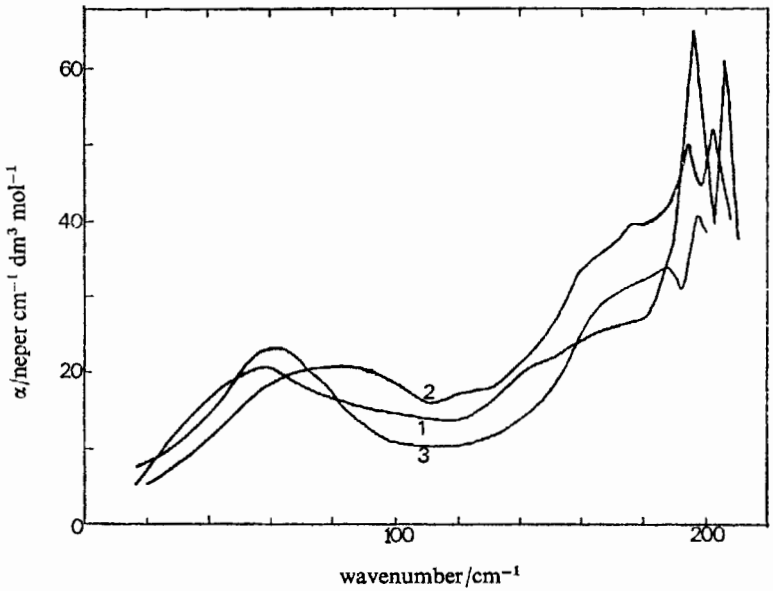


FIG. 1.—Absorption coefficient against wavenumber for (1) $Fe(AcAc)_3$, (2) $Cr(AcAc)_3$ and (3) $Zr(AcAc)_4$ in benzene.

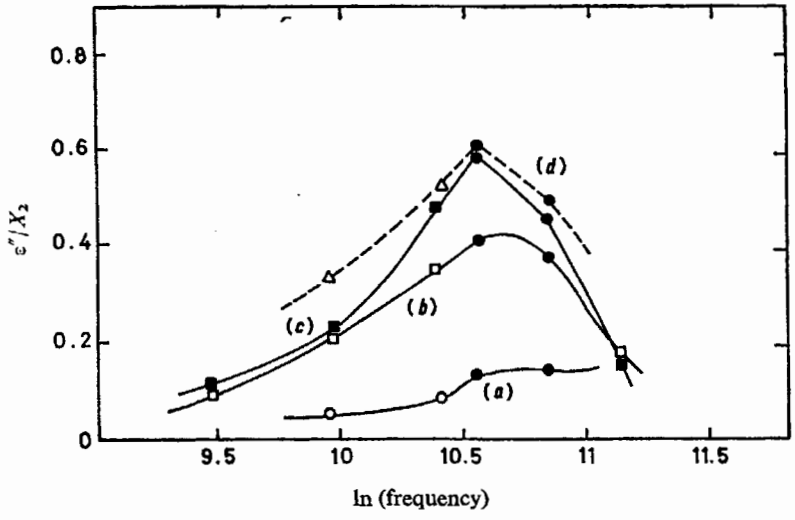


FIG. 2.—Microwave loss measurements taken at room temperature together with the results of other workers for (*a*) $Be(AcAc)_2$, (*b*) $Al(AcAc)_3$, (*c*) $Cr(AcAc)_3$ and (*d*) $Fe(AcAc)_3$. ●, present work; ○, DiCarlo *et al.* (1973); △, ref. (6); □, ■, ref. (7).

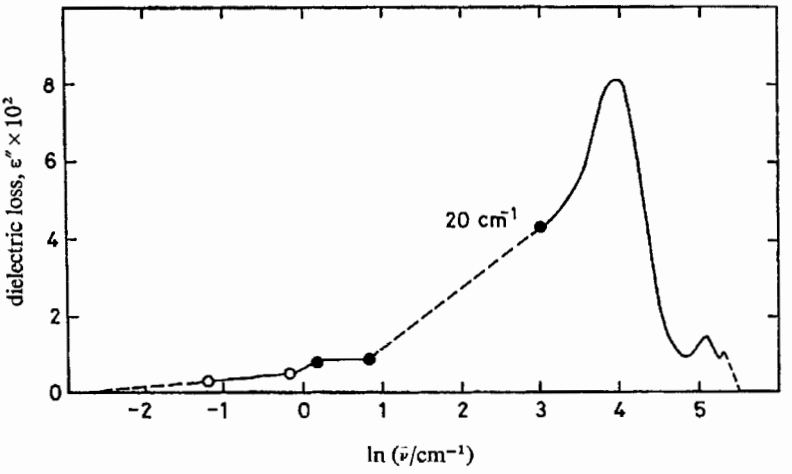


FIG. 3.—Plot of loss factor $\varepsilon''(\bar{\nu})$ against ln wavenumber for beryllium (II) bis-acetylacetonate. m = 0.6653, x = 0.063 89. ●, present work; ○, DiCarlo *et al.* (1973).

TABLE 1.—MICROWAVE AND FAR INFRARED POLARISATIONS FOR METAL ACETYLACETONATES

benzene solution (corrected for solvent)	P for microwave plus far infrared to ≈ 200 cm^{-1}/cm^3	P from 2.2 mm to ≈ 200 cm^{-1} (f.i.r. peak)/cm^3	(P_{RF}–P_{vis})* (" atomic polarisation ") /cm^3
$Be(AcAc)_2$	27.2	22.8	28.0[5]
$Al(AcAc)_3$	36.4	24.3	43.0 [5]
$Cr(AcAc)_3$	40.2	26.0	42.0 [5]
$Fe(AcAc)_3$	45.8	28.2	52.0 [6]
$Zr(AcAc)_4$	49.4	23.1	62.0 [5]

* RF = radio frequency; vis = visible light frequency

Haigh *et al.*[1] call attention to the polarisations in the microwave region, but do not attempt the integration [(eqn (2)].

Not only the integrated intensity but also the position and peak heights of the ≈ 60 cm^{-1} absorption in the far infrared form a steady pattern (table 2).

The small drift in sharpness and $\bar{\nu}$(max) between Be–M^{III}–Zr could be due to different numbers of (AcAc) groups rocking or bending internally, and/or reflect the different rigidities imposed on these groups by their different numbers and central charges. There is a recurring indication of a second feature in the far infrared absorption which has been briefly alluded to above. For the Be compound there is a well defined peak at ≈ 155 cm^{-1} : α_{max} ≈ 16 neper cm^{-1} dm^3 mol^{-1}. For the Al compound a sharp peak at 178 cm^{-1} : α_{max} ≈ 33 neper cm^{-1} dm^3 mol^{-1}. Fe, a shoulder at ≈ 160 cm^{-1} : α_{max} 24 neper cm^{-1} dm^3 mol^{-1}; Cr, a shoulder at ≈ 170 cm^{-1} : α_{max} ≈ 32 neper cm^{-1} dm^3 mol^{-1}; Zr, a shoulder at 162 and 178 cm^{-1} : α_{max} ≈ 35 neper cm^{-1} dm^3 mol^{-1}.

In the above sequence the $Al(AcAc)_3$ band at 178 cm^{-1} is an anomalous member of the series but there is a fair amount of evidence to support the tentative hypothesis that there is a second bending type mode of (AcAc) near 170 cm^{-1}. Both this and the 60 cm^{-1} feature are thus specific contributions to the " anomalous " atomic polarisation, which partly arises therefore from standard infrared intramolecular type absorption occurring at long wavelengths in the submillimetre region.

Below 5 cm^{-1} the microwave absorptions give (by reference to table 1)

	$Be(AcAc)_2$	$Al(AcAc)_3$	$Fe(AcAc)_3$	$Cr(AcAc)_3$	$Zr(AcAc)_4$
$P_{microwave}$	4.4	12.1	14.2	17.6	26.3

The origin of this microwave part of the overall polarization, the only uncertainty remaining, may be attributable to the following: (*a*) The (AcAc) groups may not be so symmetrised in their solution configuration as to balance out their permanent dipolar contributions. The absorptions would then be attributable to a conventional Debye relaxation process.[3, 4] (*b*) Interaction induced absorption.[5] (*c*) There may always be a very low frequency distortion mode in the microwave region.[6, 7]

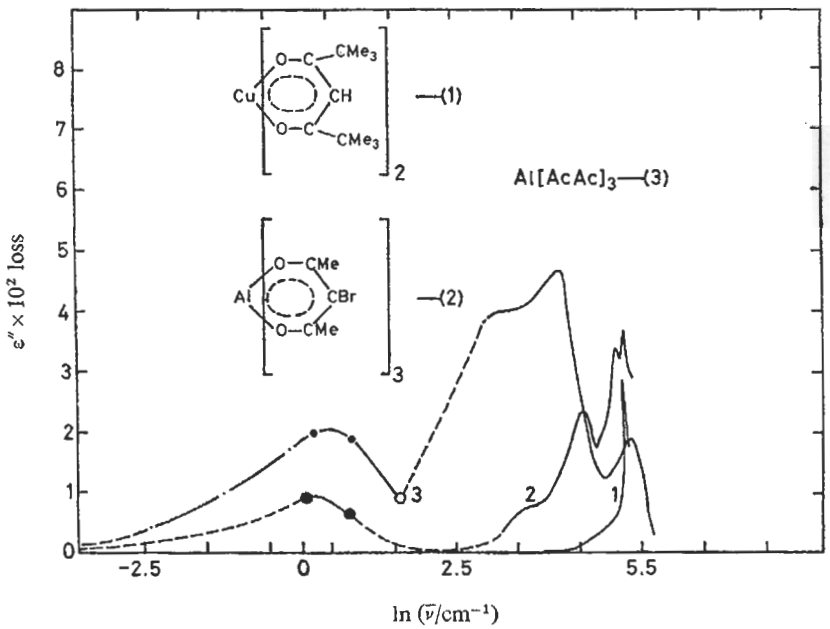


FIG. 4.—Plot of loss factor $\varepsilon''(\bar{\nu})$ against ln (wavenumber) for (1) copper (II) bis 1,5-trimethyl-2,4-pentane dionate; (2) aluminium (III) tri-3-bromo-2,4-pentane dionate; (3) aluminium (III) tri-acetylacetonate.

Further insight is gained by an analysis of substituted acetylacetonates. Difficulties arise because of the lower solubilities of these compounds in benzene compared with the parent substance. However, we have started such an investigation and present some preliminary results. Several interesting observations arise. The substitution of Br for H, in two of these complexes, lowers their atomic polarisations. In aluminium (III) triacetylacetonate the change is a pronounced one from 43 to $\approx$ 16 cm^3. The microwave and far infrared contributions to P_{at} are estimated at

TABLE 2.—FEATURES OF THE 60 cm^{-1} ABSORPTION OF THE METAL ACETYL ACETONATES

	$Be(AcAc)_2$	$Al(AcAc)_3$	$Fe(AcAc)_3$	$Cr(AcAc)_3$	$Zr(AcAc)_4$
$\bar{\nu}$(max)/cm^{-1}	55	62	60	60	80
α(max) /neper cm^{-1} dm^3 mol^{-1}	29	25	23	24	22

5 cm^3 and 8.7 cm^3, respectively (fig. 4). Substitution of t-butyl for $-CH_3$ groups removes the low frequency absorption in the far infrared, only absorptions near 200 cm^{-1} remaining (fig. 4).

This strongly suggests that these long wavelength bands are intramolecular modes associated with the acetyl acetonate groups and arising from bending motions of the chelate rings about the O . . . O vectors.[4]

We thank the S.R.C. for an equipment grant and a fellowship to G. J. E., the Ramsay Memorial Trust for the 1976-78 Fellowship to M. W. E. and De Pauw University for the grant of sabbatical leave and travel funds to E. S.

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(PAPER 8/1964)