The Electric Polarisations of some Metal Acetylacetonates at 29.7 cm^{-1}

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Summary Electric polarisations at 29·7 cm^{-1} of the acetylacetonates of Fe^{III}, Cr^{III}, Mn^{III}, Co^{III}, Al^{III}, and Th^{IV} confirm that there is a large dispersion at lower frequencies which seems, however, not to be due to a simple, single Debye-type relaxation process.

THE electric polarisations of metal acetylacetonates, measured in solution, show the interesting feature of a relaxation at a frequency which is too high for a dipole rotation but surprisingly low for a vibratory process.[1] The development of the HCN maser,[2] giving radiation at 29·7 cm^{-1}, makes possible accurate measurements in the very far i.r.

Nelson and White[3] recently reported that the total polarisation of aluminium acetylacetonate in benzene solution at 29·7 cm^{-1} is 107·05 cm^{3}mole^{-1}. We have measured this quantity for six metal acetylacetonates [M(acac)$_3$: M = Fe^{III}, Cr^{III}, Mn^{III}, Co^{III}, Al^{III}; M(acac)$_4$: M = Th^{IV}] in benzene solution using a continuous-wave HCN maser source and a phase-modulated Mach–Zehnder interferometer[4] with Golay detector. Refractive indices in solution may be measured to typically ±0·0002 (Nelson and White[3] quote an uncertainty of ± 0·004). Values are listed in the Table, column 4. Columns 1 and 2 give the values observed in the gas phase[5] (at the temperature stated) and in solution[6] (at 25°), at radio frequencies. Column 3 gives values extrapolated by us from the recent microwave data of DiCarlo, Stronski, and Varga,[1b] using their calculated relaxation times and assuming a Debye exponential damping process for the relaxation. Nelson and White's value for the Al^{III} compound agrees with ours within experimental error.

Polarisations of metal acetylacetonates cm^3 mole^{-1}

Metal	Gas phase radio freq.	Solution radio freq.	Solution micro-wave extrapol. to 29·7 cm^{-1}	Solution experimental 29·7 cm^{-1}	Solution 17,300 cm^{-1}
Be^{II}	86·0 (185—255°)	87·34	—	—	59·4
Al^{III}	130·8 (229—247°)	134·0	122	109	91·1
Cr^{III}	135·5 (236—247°)	137·5	125	115	95·3
Mn^{III}	—	174*	159	122	—
Fe^{III}	146·6 (229°)	148·6	131	119	91·5
Co^{III}	—	129·5	121	122	99·4
Th^{IV}	(200) (238°)	195·6	—	179	127·5

* Mr. G. J. Rowlands, personal communication.

It will be noted that

(i) the radio-frequency polarisations in the gas phase and in solution agree to within 2—4 cm^{3}mole^{-1}, the former being generally the lower.

(ii) The polarisations at 29·7 cm^{-1} are much lower than these, but not down to the values found for visible wavenumbers. (Table, column 5.)

(iii) The observed values at 29·7 cm^{-1} are less than those from the microwave extrapolation except for the Co^{III} compound. The Mn^{III} compound is especially low. In general, therefore, the dispersion curve appears not to be a simple Debye-type one.

Nelson and White have suggested that the chelate rings have minimum potential energy when the metal atom is somewhat displaced from the plane of the three carbon and two oxygen atoms; *i.e.* that each ring has two minima of potential energy *vs* conformation. They appear to suggest further that an asymmetric, and therefore polar, conformation is produced by a slowly changing solvent cage. An applied electric field would favour one inverted form. The relaxation time would then be related to the lifetime of the cage.

We comment that

(iv) while *X*-ray data may *permit* the postulation of bent chelate rings[7] they appear not to *require* this,

(v) inversion between two polar conformations corresponding to different potential wells gives a low-frequency polarisation which is proportional to $1/T$. The drop of such polarisation from room temperature to *ca.* 500°K is, therefore, about 40%. From the differences between radio and sub-millimetre frequency values, at 300°K, of 21, 27, and 20 cm^{3}mole^{-1} for the Al^{III}, Fe^{III}, and Cr^{III} complexes (columns 2 and 3) falls of 8—10 cm^{3}mole^{-1} would then be predicted at 500°K. These are much larger than the differences actually observed [see (i) above].

(vi) There is no evidence that the high polarisations at radio frequency are unique to the condensed phase.[5,6] While one might like to see the gas phase polarisations re-examined with improved apparatus, the pattern of results was very definite and not at all what had been expected from the solvent-effect theory originally suggested by Frank and Sutton.[8]

Motion of the chelate rings may well be relevant to the relaxation process under discussion, but the observations (v) and (vi) above can be explained on the hypothesis that each chelate ring has minimum potential energy when all its atoms are coplanar, and that it oscillates in simple harmonic motion about this plane. We have observed no absorption in the vapour phase from 100 cm^{-1} down to about 30 cm^{-1} [9] in the Cr^{III}, Fe^{III}, and Th^{IV} compounds.

This simple hypothesis does not explain what little is known about the dispersion curves which seem compatible with an aperiodic process that is affected by temperature, roughly as if controlled by liquid viscosity,[1] but is not a simple, single Debye-type process [see (iii) above]. However:

(vii) because the chelate rings are large and peripheral their vibrations might be highly damped by collisions. This would greatly modify the dispersion curve but would not affect the polarisations at high- and low-frequency limits.

(viii) If the potential function contained positive anharmonic terms there would be some fall of radio-frequency polarisation with rise of temperature[5] and some increase in the vibration frequency. Were there a solvent cage this would also, by definition, modify the potential function.

(ix) Asymmetric distortions by the applied field of the cage of oxygen atoms round the central metal atom would probably make large contributions to the polarisation which might vary from one compound to another [*cf.* (iii) above].

Further information about the dispersion curves is essential. The effects of solvent on polarisations at 29·7 cm^{-1} are being investigated, and measurements of absorption over a range of frequency about this value are being made.

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