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Charge-exchange reactions should be a convenient method of observing the spectra of molecular ions that are unstable in electrical discharges. Further work is in progress.

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# Hypersensitive Transitions in Rare-Earth Ions

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A FEW years ago, it was noticed that the intensities of some absorption lines in the solution spectra of rare-earth ions are peculiarly sensitive to the solvent.[1] The source for the hypersensitivity was later studied in detail.[2] The selection rules for the lines in question, which all correspond to transitions within the $4f$ shell, are identical to those for pure quadrupole radiation; but the calculations revealed that the observed intensities are much too large by several orders of magnitude for this to be the explanation. Dynamic mechanisms depending on vibrations in the liquid were also rejected, as were sources depending on variations of covalency. It was concluded that the hypersensitivity owed its existence to the inhomogeneous polarizability of the solvent, which was visualized as enhancing the variation of the electric vector of the electromagnetic radiation across a rare-earth ion, thereby greatly increasing the intensities of quadrupole transitions.

Subsequent work has tacitly accepted this explanation,[3] though some scepticism has recently been expressed.[4] The purpose of this note is to air a certain uneasiness in the previous analysis[2] and, in particular, to point out a new source for the hypersensitivity.

To obtain changes in intensity of lines satisfying quadrupole selection rules, it would only be necessary to vary the amplitudes of terms of the type $Y_{1m}$ in the electric potential of the complex surrounding a rare-earth ion. These terms permit forced electric-dipole transitions and the combination of $Y_{1m}$ with the dipole operator reduces to an effective quadrupole operator within the $4f$ shell. However, there is a classic argument for excluding the harmonics $Y_{1m}$ from the Hamiltonian. Unlike all $Y_{km}$ with $k>1$, they possess nonvanishing derivatives at the origin, namely, the nucleus of the rare-earth ion. This implies the existence of an electric field at the nucleus, and hence that the rare-earth ion and its complex are not in equilibrium. Any static model, it seems, would necessarily have to exclude them and, for this reason, they were rejected in previous work.[1,2] However, this argument overlooks the fact that the electrons of the rare-earth ion may also produce an electric field at the nucleus that exactly cancels that coming from the neighboring ions. Evidently this asymmetrical electronic distribution within the rare-earth ion can be regarded as being produced by the external electric field; so, for calculating the mixing of the $4f$ orbitals with those of opposite parity, the terms $Y_{1m}$ should be included in the Hamiltonian. Of course, not all arrangements of solvent molecules around the central rare-earth ion produce such terms. In Table I, the 32 point symmetries are divided into those that (a) possess no harmonics $Y_{km}$ with $k$ odd; (b) possess some harmonics $Y_{km}$ with $k$ odd, but none with $k=1$; (c) possess harmonics $Y_{km}$ with $k=1$. (This table is constructed from Table 5 of Prather.[5]) On this basis, an enhanced pseudoquadrupole transition would indicate a symmetry type falling only into Category (c); and, from the estimates of the dynamic effects,[2] it would be necessary to assign this symmetry to the nearest neighbors to reproduce an order of magnitude change in the intensity. This does not rule out the mechanism depending on quadrupolar enhancement by dielectric inhomogeneity, which must, of course, contribute to some extent; but assigning the hypersensitivity principally to a simple change of point symmetry seems much more plausible.

TABLE I. Classification of point groups.

| | |
|---|---|
| (a) | $C_i$, $C_{2h}$, $C_{4h}$, $C_{6h}$, $D_{2h}$, $D_{4h}$, $D_{6h}$, $D_{3d}$, $S_6$, $O$, $O_h$, $T_h$. |
| (b) | $D_2$, $D_{2d}$, $D_3$, $D_{3h}$, $D_4$, $D_6$, $C_{3h}$, $S_4$, $T$, $T_d$. |
| (c) | $C_s$, $C_1$, $C_2$, $C_{2v}$, $C_3$, $C_{3v}$, $C_4$, $C_{4v}$, $C_6$, $C_{6v}$. |

It is interesting to note that the rare-earth double nitrates possess the point symmetry $C_{3v}$ at a rare-earth site.[6] On the present theory, but not necessarily on that depending on pseudoquadrupole transitions, we would expect the hypersensitive lines to be enhanced relative to the others. It is thus significant that the lines at 17 300 and 19 320 $\mathrm{cm}^{-1}$ in $\mathrm{Nd}^{3+}$, already classed as hypersensitive,[1] appear to be the most intense in the absorption spectrum of $\mathrm{Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O}$.[7]

Finally, it is to be noted that for $\mathrm{Sm}^{2+}$ at a site of $C_{4v}$ symmetry in BaClF, there appears to be very strong evidence for terms of the type $Y_{1m}$ in the Hamiltonian.[8] This is consistent with the classification in Table I.

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# Vibrational Relaxation and Volume Viscosity in Carbon Tetrachloride*

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RECENTLY a number of investigations of the velocity of sound in the kilomegacycle-per-second region by means of new techniques have been reported. These data have considerably greater precision than obtained with earlier techniques. Of particular interest are data in carbon tetrachloride,[1–5] which taken altogether indicate the presence in the kilomegacycle-per-second region of dispersion due to vibrational relaxation. The relationships between velocity, absorption, and thermodynamic parameters needed to evaluate these high-frequency data have been given by Herzfeld and Litovitz.[6] The equations used below may be obtained from expressions derived in Ref. 6.

Sette, Busala, and Hubbard[7] carried out measurements of ultrasonic velocity in $CCl_4$ vapor. They found a relaxation process in which the entire vibrational specific heat relaxed with a single relaxational frequency. The total dispersion to be expected in liquid $CCl_4$ can be calculated from the expression

$$V_\infty^2/V_0^2=[(C_P-C')C_V]/[(C_V-C')C_P], \quad (1)$$

where $V_\infty$ and $V_0$ are the high- and low-frequency velocities, $C_P$ and $C_V$ are the specific heats at constant pressure and volume, and $C'$ is the vibrational specific heat. In order to calculate the fraction of this dispersion expected at a given frequency, it is necessary to calculate $\tau''$ from the following equation:

$$\tau''=(\alpha_{\mathrm{vib}}/f^2)_{\mathrm{low}}[C_P(C_V-C')V_0]/[2\pi^2C'(C_P-C_V)], \quad (2)$$

where the low-frequency vibrational absorption $(\alpha_{\mathrm{vib}}/f^2)_{\mathrm{low}}$ may be obtained by subtracting the portion due to viscous losses from the total absorption. It was first assumed that $\eta_v=\frac{4}{3}\eta_s$ in $CCl_4$, as in many liquids where $\eta_v$ and $\eta_s$ are the volume and shear viscosities, respectively; therefore $\alpha_{\mathrm{vis}}$ becomes $0.08\ \alpha_{\mathrm{total}}$.[8] Using this estimate, $\tau''$ was found to be $5\times10^{-11}$ sec and using the following expression the dispersion curve was calculated and plotted in Fig. 1:

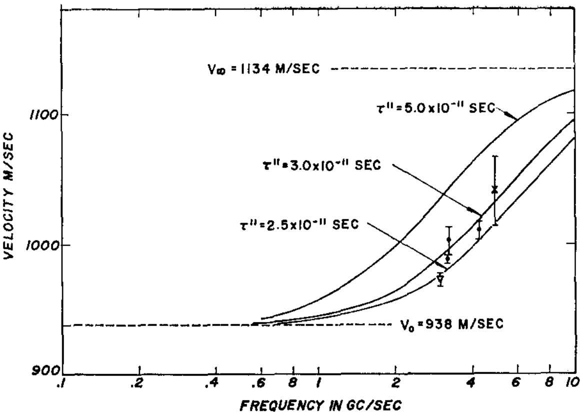

FIG. 1. Dispersion curves for $CCl_4$ at 20°C. Radiation impedance (▽), laser (●), nonlaser optical (×).

$$\frac{V^2}{V_0^2}=1+\frac{(C_P-C_V)C'}{C_P(C_V-C')}\frac{\omega^2\tau''^2}{1+\omega^2\tau''^2}. \quad (3)$$

It is obvious that the velocity dispersion calculated in this manner does not agree with data in the kilomegacycle-per-second region. Since these data are based on two different techniques and five different investigators it seems most probable that the assumption $(\eta_v=\frac{4}{3}\eta_s)$ made in order to calculate $\tau''$ is incorrect. From Fig. 1 it is clear that for values of $\tau''$ in the range $2.5\times10^{-11}$ to $3\times10^{-11}$ sec good agreement is obtained. This leads to a value of $\eta_v/\eta_s$ between 14 and 18 which is a surprisingly large value.

Of interest is the fact that in the molten chlorides[9] (e.g., LiCl, NaCl, KCl, CsCl, and AgCl) the ratio $\eta_v/\eta_s$ is also large (approximately 20). It is an odd (and no doubt fortuitous) result that quite dissimilar chloride compounds should exhibit such similar high values of $\eta_v/\eta_s$.

It should be pointed out that Mash *et al.*[10] have recently reported an absorption measurement in $CCl_4$ at 3.2 kMc/sec. The value of total absorption obtained by them agrees closely with that calculated on the basis of the assumption $\eta_v=\eta_s$. This is, however, a single measurement of absorption for which no experimental details are given. Additional information and measurements are needed in order to resolve the discrepancy between velocity and absorption data.

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