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Raman Intensities and Metal–Metal Bond Orders[1]

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Absolute Raman intensities and molecular polarizability derivatives are reported for the metal–metal stretching modes of Hg_2^{2+}, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$, as well as for the totally symmetric "cluster" modes of $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl_4(OC_2H_5)_4$. A resonance Raman effect has been observed for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, and the measured molecular polarizability derivatives for these species have been extrapolated to zero exciting frequency. Metal–metal bond polarizability derivatives have been calculated with the aid of eigenvectors obtained from previous normal-coordinate analyses. Their values are interpreted with the aid of the δ-function model equation of Long and Plane. The conclusion emerges that weak metal–metal interactions, on the order of 0.1 electron or less per metal–metal "bond," are sufficient to account for the Raman intensities of the Bi(III), Pb(II), and Tl(I) complexes. That the interaction is nevertheless significant is indicated by comparison with Raman intensities for polynuclear complexes of the d^0 metal ions Nb(V) and Ta(V). It appears that Raman spectroscopy is a sensitive probe for metal–metal interaction. The calculated bond orders for Hg_2^{2+}, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$, while of the right order of magnitude, are not entirely satisfactory with respect either to absolute or relative values and expose certain limitations in current theory.

Introduction

It has been emphasized[2] that in applying Raman spectroscopy to problems of molecular structure and bonding, one can obtain valuable information not only from the frequencies of the observed vibrational bands but also from their intensities. In favorable cases one can hope to estimate bond orders from measured Raman intensities. We report here results of an initial study aimed at using such measurements to obtain relative orders for bonds between metal atoms in polynuclear complexes.

Potentially, Raman intensities have great utility in the study of metal–metal bonds. Crystallographic structure determinations demonstrate a wide variability in the lengths of metal–metal bonds and, therefore, presumably in their strength. Furthermore, in a large fraction of polynuclear structures the metal atoms are connected by bridging ligands. It is then a matter of conjecture whether there exists, in addition, a direct bonding interaction between the metals. Standard criteria of bonding—chemical stability, internuclear distance, magnetism—often give ambiguous answers in such cases. New approaches are needed, and it is in this context that Raman intensity measurements may be of particular interest.

Included in this study are three bridged complexes $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl_4(OC_2H_5)_4$ which contain octahedral or tetrahedral arrays of metal atoms. Qualitative Raman intensity arguments have been presented[3] in favor of metal–metal interaction in these species. Such interaction is expected to be weak at best in view of the large internuclear distances involved[3] (3.7–3.8 Å) and the stability of the $5d^{10}s^2$ valence state of the metal ions. It is therefore a matter of considerable interest to set the Raman intensity argument on a quantitative basis. For comparison we have measured Raman intensities for the unequivocally metal–metal bonded compounds Hg_2^{2+}, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$.

Intensities and Bond Polarizability Derivatives

The theory of Raman intensities and its application to problems of chemical bonding has been reviewed by Hester.[2] For a system of freely rotating molecules (gases or liquids) the observed intensity for a totally symmetric (A_1) Raman line is given by[2]

$$I = \frac{K\bar{M}(\nu_0 - \nu_i)^4\left[45\left(\dfrac{\partial\bar{\alpha}}{\partial Q_i}\right)^2\right]}{\nu_i[1 - \exp(h\nu_i/kT)]}\left(\frac{6}{6 - 7\rho}\right) \qquad (1)$$

where K is a constant, $\bar{M}$ is the molar concentration of the scattering species, ν_0 is the frequency of the exciting radiation, ν_i and Q_i are the frequency and the nomal coordinate of the ith normal mode, $\bar{\alpha}$ is the mean molecular polarizability, and ρ is the depolarization ratio of the spectral line. Thus, measurement of the intensity of a Raman line allows the calculation of the mean molecular polarizability derivative.

In order to relate Raman intensities to bond properties one would like to divide molecular polarizability derivatives into contributions from individual bonds. A simple method for doing this was first proposed by Wolkenstein[4] and later formalized by Long.[5] It is based on the assumption that the elements of the molecular polarizability tensor are given by a superposition of the principal polarizability components of individual bonds. For example

$$\alpha_{xy} = \sum_u\sum_v \alpha_{uv}(Xuv)(Yuv) \qquad (2)$$

where α_{uv} is the vth principal component ($v = 1, 2, 3$) of the polarizability of the uth bond and (Xuv) is the direction cosine between the particular vth axis and the X axis. Using the orthonormality relations for direc-

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[1] This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences, and by National Science Foundation Grant GP-10122.

[2] R. E. Hester in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, Chapter 4.

[3] V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 193 (1968).

[4] M. Wolkenstein, *Dokl. Akad. Nauk SSSR*, **30**, 791 (1941).

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tion cosines one can relate the mean values of the molecular and bond polarizability tensors

$$\bar{\alpha} = \sum_u \bar{\alpha}_u \qquad (3)$$

This expression may be differentiated with respect to the normal coordinates, which in turn are related to internal coordinates by $\vec{R} = L\vec{Q}$, where L is the matrix of eigenvectors for the normal vibrations. On the assumption that $\bar{\alpha}_u$ depends only on the stretching of bond u, it follows that

$$\frac{\partial \bar{\alpha}}{\partial Q_i} = \sum_u l_{ui} \frac{\partial \bar{\alpha}_u}{\partial R_u} \qquad (4)$$

where l_{ui} is the L matrix element between R_u and Q_i. This simple procedure, therefore, yields a set of linear equations (one for each A_1 normal mode) with which the individual mean bond polarizability derivatives may be calculated.

The solution of the above equations is often ambiguous since only the magnitude (but not the sign) of the polarizability derivative is known. Of the various solutions, there may be more than one which is physically reasonable. Furthermore, for complicated molecules it is often impossible to resolve fully and to measure accurately all of the A_1 Raman bands. If however, the normal mode is primarily composed of only one type of valence stretch (*i.e.*, a "group frequency"), the problem is simplified considerably. In this case, all elements, l_{ui}, for valence stretches which are not in the characteristic group are nearly zero. Terms involving them may therefore be neglected in eq 4 and the summation over u gives

$$\frac{\partial \bar{\alpha}}{\partial Q_i} = N_u l_{ui} \frac{\partial \bar{\alpha}_u}{\partial R_u} \qquad (5)$$

where N_u is the number of characteristic valence bonds. If there is only one A_1 normal mode, or if the normal mode is completely characteristic, the l_{ui} may be calculated by $l_{ui} = (G_{ii}/N_u)^{1/2}$, where G_{ii} is the appropriate A_1 symmetry G matrix element.[6] Since vibrations are rarely completely decoupled, it is significantly more accurate to use l_{ui} values obtained from a normal-coordinate analysis.

The above treatment of Raman intensities is based upon a number of assumptions. The Wolkenstein theory requires (1) that molecular polarizability is a superposition of bond polarizabilities, (2) bond polarizabilities are independent of the relative orientation of the bonds, and (3) a bond polarizability does not depend on the stretching of other bonds. The first two of these seem to be reasonably valid.[7,8] The third is difficult to test but the evidence suggests that it may fail for molecules with extensive electron delocalization.[9]

The simple polarizability theory of Placzek,[10] from which the original intensity equation is derived, assumes that the frequency of the exciting radiation is much smaller than any electronic absorption frequency. If this is not the case, the Raman intensity (and any calculated polarizability derivative) may be greatly enhanced due to the resonance Raman effect.[11] Unfortunately, many molecules with metal–metal bonds (in our case $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$) have absorption maxima relatively close to the frequencies usually used for Raman excitation. To allow for resonance effects, one can measure intensities as a function of the excitation frequency and extrapolate to a frequency at which the polarizability theory is valid.

Experimental Section

Chemicals.—Hydrolyzed lead(II) and bismuth(III) solutions were prepared by dissolving the reagent grade metal oxides in concentrated perchloric acid with overnight digestion. The solutions were analyzed for metal content by titration with standard EDTA.[12] Total perchlorate was determined by passing the solutions through a cation-exchange resin in the acid form and titrating the liberated acid. Thallous ethoxide was prepared as described in the literature.[13] Mercurous ion solutions were prepared by dissolving freshly opened reagent mercurous nitrate in standardized perchloric acid. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Strem Chemicals, Inc., and used as received. Solutions of $Tl_4(OC_2H_5)_4$, $Mn_2(CO)_{12}$, and $Re_2(CO)_{10}$ were prepared by dissolution into weighted amounts of fresh spectral grade carbon tetrachloride.

Spectrometer.—Raman spectra were recorded with a spectrometer designed and built in this laboratory.[14] In this instrument scattered light, excited by a focused He–Ne Laser beam, is collected at 90° by a *f*/1.2 lens and focused into a Spex Model 1400 double monochromator through a polarization scrambler. The dc signal from a cooled ITT FW-130 Startracker phototude is amplified and displayed on a strip-chart recorder. The wavelength was calibrated using neon and argon discharge lines. The relative spectral response of the system was determined by recording the spectrum of a quartz–iodine lamp as described in the literature.[15]

Intensity Measurements.—Raman intensities were measured in all cases by using an internal standard. The standard chosen for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $Tl_4(OC_2H_5)_4$ was the ν_1 (A_1) line of the solvent, CCl_4. The standard for the aqueous solutions of Hg_2^{2+}, $Bi_6(OH)_{12}^{6+}$, and $Pb_4(OH)_4^{4+}$ was ν_1 (A_1) of perchlorate ion.

The line of interest and the standard line were recorded first with the laser light polarized perpendicular to the direction of observation. The laser polarization was then rotated until parallel to the monochromator axis and the two lines were again recorded using identical instrumental conditions. This procedure was repeated at least three times for each solution. The areas of the Raman bands for the $Mn_2(CO)_{10}$ solutions were measured directly with a polar planimeter. For the $Re_2(CO)_{10}$ solutions, direct integration of the metal–metal band at 120 cm^{-1} was difficult since this band was not fully resolved from the broad envelope of metal–carbon deformation modes. An approximate measure of the area was obtained with the aid of a Du Pont Model

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TABLE I

Molecule (solvent)	$\nu^{A_1}{}_{M-M}$, cm^{-1}	R_{mol}[a]	ρ	$\bar{\alpha}_Q'$, Å^2	$\bar{\alpha}_u'$, Å^2	$\bar{\alpha}_u'/r^3$	$n/2$[b]
$Hg_2(H_2O)_2^{2+}$ (aqueous ClO_4^-)	180	3.46	0.28	0.433	4.65	0.287	0.38
$Mn_2(CO)_{10}$ (CCl_4)	160	10.8	0.40	0.723	5.35	0.215	0.95
				(0.50)[c]	(3.70)	(0.149)	(0.66)
$Re_2(CO)_{10}$ (CCl_4)	120	2.60	0.37	0.286	3.14	0.114	0.52
				(0.20)[c]	(2.20)	(0.080)	(0.36)
$Bi_6(OH)_{12}^{6+}$ (aqueous ClO_4^-)	180	3.31	0.0	0.480	1.01	0.020	0.061
$Pb_4(OH)_4^{4+}$ (aqueous ClO_4^-)	130	0.60	0.0	0.154	0.49	0.009	0.023
$Tl_4(OC_2H_5)_4$ (CCl_4)	100	0.46	0.0	0.137	0.44	0.008	0.016

[a] Relative molar intensity. [b] From eq 6. [c] Figures in parentheses are based on molecular polarizability derivatives extrapolated to zero exciting frequency (see text).

310 curve resolver by fitting the bands with a Lorentzian line shape. Areas measured in this manner were reasonably consistent and were considered more accurate than those obtained by drawing an arbitrary base line for the partially resolved band. The measured relative intensities were averaged, corrected for instrumental response, and then used to calculate relative polarizability derivatives.

To check for resonance effects, fresh $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ solutions were measured using a mixed-gas Ar–Kr ion laser (Coherent Radiation Laboratory Model 52 and Carson Laboratory Model 10SP) which offers many lines from 4880 to 6764 Å for excitation. Thus, the relative molar intensity for the metal–metal band of each compound was obtained as a function of excitation frequency.

Results and Discussion

The results of the intensity measurements with 6328-Å excitation are presented in Table I along with a number of calculated parameters to be discussed below. Molecular polarizability derivatives were calculated using eq 1. They were put on an absolute scale using $\bar{\alpha}_Q'$ values of 0.685 and 0.865 Å^2 for CCl_4[16] and ClO_4^-,[17] respectively.

Resonance Raman Effect for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.—Figure 1 shows the relative molar intensities for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ as a function of excitation frequency. It is evident that we are dealing with a resonance Raman effect. The greater effect observed for $Mn_2(CO)_{10}$ than for $Re_2(CO)_{10}$ is consistent with the order of frequencies for the first electronic transition: 28,990 and 32,260 cm^{-1}, respectively. Furthermore the intensity increase for the metal–metal stretching bands is consistent with the assignment by Levenson and Gray[18] of the first electronic absorption to a $\sigma \rightarrow \sigma^*$ transition involving electrons primarily in the metal–metal bond. It is expected that those normal modes which are vibronically active in the electronic transition should exhibit enhancement of their Raman intensity.[19]

In order to obtain valid polarizability derivatives, the data must be extrapolated to an excitation frequency (namely, zero) at which the polarizability theory is meaningful. The data are highly nonlinear so that a direct extrapolation of the molar intensities as a function of excitation frequency is uncertain. Although there is not, as yet, a fully tested simple theory to account for the frequency dependence of Raman intensities, the work of Albrecht[19] and Behringer[11] leads one to expect a frequency dependence for $\bar{\alpha}_Q'$ of the form

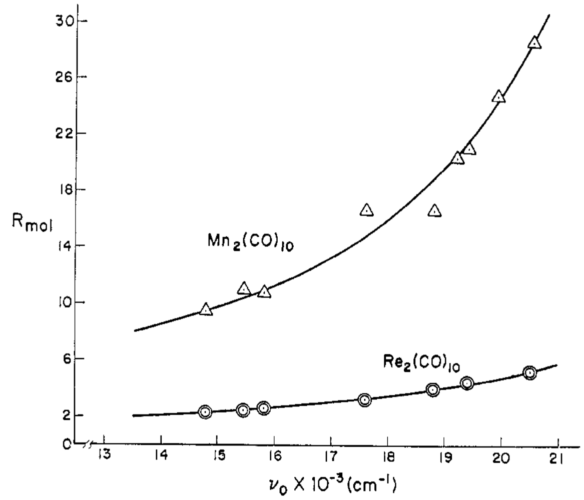

Figure 1.—Relative molar intensity *vs.* Ar–Kr laser excitation frequency for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The intensity standard is the ν_1 (A_1) line of the solvent, CCl_4.

$$\frac{(\nu_e^2 + \nu_0^2)}{(\nu_e^2 - \nu_0^2)^2}$$

where ν_e is an effective absorption frequency and ν_0 is the exciting frequency. Assuming that the internal standard shows no resonance effects, $\bar{\alpha}_Q'$ determined by relative measurement should show a similar dependence upon exciting frequency.

Figure 2 shows the calculated molecular polarizability derivatives for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ plotted against the function $X = (1 + (\nu_0/\nu_e)^2)/(1 - (\nu_0/\nu_e)^2)^2$ which is equivalent to that given above. The experimentally observed absorption maxima were chosen as effective absorption frequencies. In this form the data are indeed linear and permit easy extrapolation to $X = 1.0$ (the value of the ordinate for $\nu_0 = 0$). Polarizability derivatives obtained in this way are given in parentheses in Table I.

It must be emphasized that the above procedure is not unique. The linearity of the data is not particularly sensitive to the choice of the parameter ν_e. For instance, its value may be adjusted to force a linear extrapolation through the origin. In this case the $\bar{\alpha}_Q'$ values at $X = 1.0$ decrease by about 20%. The

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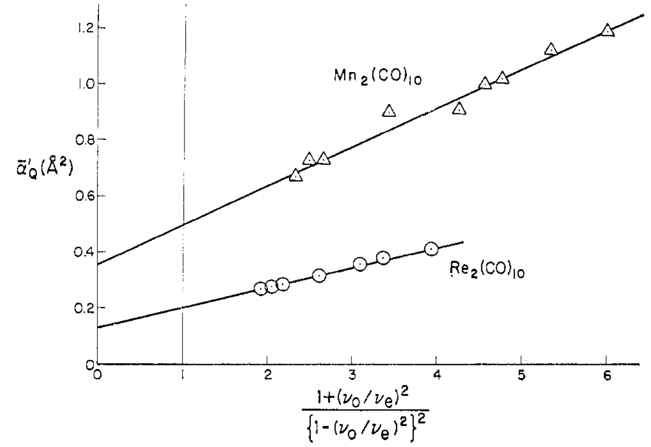

Figure 2.—Molecular polarizability derivatives, $\bar{\alpha}_Q'$, for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ *vs.* $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$. ν_0 is the laser excitation frequency; ν_e is the effective absorption frequency; ν_e = 28,990 cm^{-1} for $Mn_2(CO)_{10}$ and 32,260 cm^{-1} for $Re_2(CO)_{10}$.

ratio of the $\bar{\alpha}_Q'$ values is not greatly affected, however. In the absence of any criterion other than linearity for fixing ν_e, it seems reasonable to choose the observed electronic band maxima. The correction to the $\bar{\alpha}_Q'$ values determined from the intensities measured at 6328-Å excitation amounts to about 30% for both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

Bond Polarizability Derivatives.—Bond polarizability derivatives, $\bar{\alpha}_u'$, were calculated from $\bar{\alpha}_Q'$ using eq 5. Appropriate eigenvectors were taken from previous normal-coordinate analyses,[3,20–22] except for $Hg_2(H_2O)_2^{2+}$, for which they were calculated by standard methods[6] using the force constants given by Gager, *et al.*[23] In all cases, only the contribution of metal–metal stretching was considered. Sample calculations in which reasonable values of $\bar{\alpha}_u'$ for metal–ligand bonds, together with their associated l_{ui} values, were included in eq 4 showed that their contributions were indeed negligible.

To interpret the results we made use of a semiempirical equation recently proposed by Long and Plane,[24] which successfully predicts $\bar{\alpha}_u'$ for a wide range of compounds. In their treatment a δ-function potential model is used to derive an expression for $\alpha_{\|b}$, the parallel component of the contribution to the molecular polarizability arising from electrons in a bond. It is assumed that $\bar{\alpha}_u'$ is obtained simply by differentiating $\alpha_{\|b}$ with respect to r, the internuclear separation; *i.e.*, no contribution is allowed either from the perpendicular polarizability components or from nonbonding electrons. The resulting equation is

$$\bar{\alpha}_u' = \frac{2}{3}(g\sigma/Za_0)\left(\frac{1}{2}n\right)r^3 \qquad (6)$$

where n is the number of electrons in the bond ($n/2$ is the bond order), a_0 is the Bohr radius, Z is the effective nuclear charge, σ is the Pauling covalent bond character, and g is the δ-function strength. The quantity g is equated with $X^{1/2}$, where X is the Pauling electronegativity, and Z is taken as the atomic number minus the number of inner-shell electrons. (For a heteronuclear bond the geometric mean of the two values is used.) The most significant aspect of this equation is its prediction of a third-power dependence of $\bar{\alpha}_u'$ on the internuclear distance. This feature, along with variations in Z and g, explains the well-known variation of $\bar{\alpha}_u'$ with the atomic number of bonded atoms.[2]

Table I lists bond polarizability derivatives, corrections for the cube of the internuclear distance, and bond orders as calculated with eq 6. The most interesting feature is the clear division between species with genuine metal–metal bonds and the bridged polynuclear complexes for which significant metal–metal bonding is not anticipated but which show "cluster-type" Raman bands. It can be seen that the bond polarizability derivatives are substantially lower for the latter species than for the former, and the distinction is greatly accentuated when the derivatives are divided by the cube of the internuclear distance. An order of magnitude separates the two groups of values and carries over to the calculated bond orders. It is apparent that the metal–metal "bonds" in $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl_4(OC_2H_5)_4$ are worth on the order of 0.1 electron or less each, if this approach is valid. The great sensitivity of Raman spectroscopy to such weak interactions is due to the large internuclear distances involved.

That the metal–metal interactions for the bridged complexes are nonetheless real is indicated by the Raman results[25] obtained for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$, in which the metal atoms are arranged in an octahedron. The metal–metal separations are 3.3 Å, yet metal–metal interaction is almost certainly ruled out since the metal ions have d^0 valence states. For these complexes the lowest frequency A_{1g} band is one of the weakest in the Raman spectrum and its intensity can be ascribed to contributions from metal–oxygen stretching. In contrast the lowest frequency $A_{1(g)}$ bands for $Bi_6(OH)_{12}^{6+}$, $Pb_4(OH)_4^{4+}$, and $Tl(OC_2H_5)_4$ are substantially stronger than the $A_{1(g)}$ bands assignable to metal–oxygen stretching.

Close examination of the calculated bond orders reveals that some problems remain with respect to the interpretation of bond polarizability derivatives. For Hg_2^{2+} a reasonable bond order might be expected to be close to unity rather than the calculated value of 0.38. Matters are only made worse, although not greatly so, by an apparent breakdown in one of the assumptions made by Long and Plane, namely, that the perpendicular component of the bond polarizability derivative is zero. If this were the case, the depolarization ratio for the Hg–Hg stretching band would be 0.50 whereas the measured ratio is 0.28. From the measured ratio one calculates a value of $\alpha_{\|}'$ which gives $n/2$ = 0.28 in the Long and Plane theory. One major source of difficulty is in the choice of Z in eq. 6. Long and Plane specify

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that Z is the atomic number minus the number of inner-shell electrons. In calculating $n/2$ we used $Z = 2$ for Hg_2^{2+}, assigning the 5d electrons to the "inner shell." The same procedure was followed by Long and Plane in calculating bond orders for tetrahalomercury(II) complexes.[24] On the other hand, it is quite possible that d electrons participate in the Hg–Hg bond, but if all ten d electrons are subtracted from the inner shell giving $Z = 12$, then the calculated bond order is 2.4.

For the Bi(III), Pb(II), and Tl(I) complexes Z was taken to be 5, 4, and 3, respectively, assigning five d electrons, but not six s electrons, to the inner shell, by analogy with Hg(I). For $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ Z was taken to be 7 considering that all the d electrons are involved in either metal–metal or metal–ligand bonds. It is evident that counting electrons in this way is rather an arbitrary procedure and constitutes a limitation on the usefulness of the Long and Plane equation. It may be that for evaluation of relative metal–metal bond orders, the parameter $\bar{\alpha}_u'/r^3$ is preferable to $n/2$.

There is also the possibility that $\bar{\alpha}_u'$ depends somewhat on the shapes of the bonding orbitals. Chantry and Plane[9] suggested that increasing s-orbital contribution to carbon–carbon single bonds decreases the associated bond polarizability derivative, and rationalized the low $\bar{\alpha}'_{C-C}$ of CH_3CN relative to that of CH_3CH_3 on this basis. Possibly the low value of $n/2$ found here for Hg_2^{2+} might also be a reflection of the s character of the Hg–Hg bonding orbital. On the other hand it should be pointed out in the case of H_2, where s-orbital involvement in the bonding is surely maximal, the $\bar{\alpha}'_{H-H}$ calculated with the Long and Plane equation is within 25% of the experimental value.[24]

The polarizability derivatives for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are puzzling. For these two molecules the internuclear distances are nearly the same, as are the electronic structures and electronegativities, so that the metal–metal bond polarizability derivatives should be directly comparable. They are clearly in the wrong order considering that the Mn–Mn bond is expected to be substantially weaker than the Re–Re bond on the basis of electron impact measurements[26] and force constant determinations.[22] Conceivably we are dealing with a breakdown in the assumption of the Wolkenstein theory that bond polarizability derivatives are independent of the stretching of other bonds. Breakdown of this assumption has previously been suggested for highly delocalized systems.[9]

In summary, we conclude that measured Raman intensities can be used to give order of magnitude estimates of metal–metal interaction and that the method is quite sensitive. On the other hand it appears that current theory is not yet adequate to place the determination of metal–metal bond orders on a quantitative basis.

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Kinetics and Mechanism of the Base-Catalyzed Exchange of Hydrogen on Hypophosphite Anion[1]

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The kinetics of the exchange of the phosphorus-bonded hydrogens in the hypophosphite anion has been studied in basic solutions, using proton nmr to follow the reaction. The exchange of $H_2PO_2^-$ follows the rate law rate $= k_{PH}(OD^-)(H_2PO_2^-)$ in D_2O and the analogous expression for $D_2PO_2^-$ in H_2O, with $k_{PH} = (3.6 \pm 0.4) \times 10^{-3}\ M^{-1}\ min^{-1}$ and $k_{PD} = (1.15 \pm 0.05) \times 10^{-3}\ M^{-1}\ min^{-1}$, both at 25°. A mechanism invoking base-assisted removal of the hydrogen from hypophosphite appears to be consistent with all of the kinetic data and with the equilibrium isotopic distribution in 50:50 atom % H–D mixed solvent.

Introduction

The acid-catalyzed exchange of the phosphorus-bonded hydrogens in hypophosphorous acid has been studied by Fratiello and Anderson[4] and by Jenkins and Yost.[5] These studies, particularly the latter, indicated the existence of an intermediate common to the exchange and reduction[6] reactions of H_3PO_2. This active hypophosphorous acid is believed to be an isomeric form of the normal structure of the acid. Studies of the exchange between the phosphorus-bonded pro-

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