Inorg. Chem. **1980**, *19*, 2825–2829

Contribution from the School of Chemical Sciences,
University of East Anglia, Norwich NR4 7TJ, England

Metal–Metal Stretching Frequencies in Metal-Cluster Complexes. Approximate Force Constant Calculations for Some Small Metal Clusters

IAN A. OXTON

Received February 29, 1980

Approximate force constant calculations have been applied to some small cluster complexes. It has been shown that, for clusters containing only first-row ligands, calculations based on the metal atom skeletons alone yield metal–metal bond stretching force constants which are in good agreement with those, where available, from more rigorous analyses. The force field developed for the treatment of transition-metal clusters contains an interaction constant associated with the stretching of adjacent metal–metal bonds which takes a value of about −8% of the corresponding principal force constant. Introduction of this empirical relationship as a constraint permits simplification of the force fields in clusters of low symmetry. The presence of a μ-bridging carbonyl ligand appears to increase the effective force constant for M–M bond stretching by approximately 50%.

Introduction

The vibrational spectroscopy of metal–metal bonded polyhedra has been relatively neglected. The literature up to 1969 has been reviewed by Spiro,[1] but more recent developments have received less attention. The main reason for this apparent lack of attention stems from the difficulty in measuring Raman spectra of transition-metal cluster complexes, where photodecomposition under laser irradiation is a frequent consequence of their highly colored nature. Greater availability of facilities for low-temperature measurement of Raman spectra together with sample-spinning devices may assist in this respect.

The work described here was prompted by an apparent need for an approximate force field which could be used to predict metal–metal stretching frequencies in metal atom polyhedra with some certainty and which would hopefully obviate the need for complete vibrational and normal-coordinate analyses in order to obtain approximate metal–metal bond stretching force constants. Previous work in this context has included a number of complete force field calculations,[2–5] and these we shall use for comparison with our simplified approach. The more common method for checking the assignment of metal–metal stretching frequencies has involved use of the so-called "simple cluster ratio". This approximation ignores all interaction force constants within the cluster and all effects due to the ligands[5] and merely derives the ratio of the cluster frequencies from the ratio of the appropriate symmetrized **G** matrix elements, viz.

$$\nu_1{}^2:\nu_2{}^2:... = G_{11}:G_{22}:... \qquad (1)$$

Thus, for example, the two metal–metal stretching frequencies in an equilateral triangular cluster would be predicted as $\nu_1(a_1'):\nu_2(e') = 2^{1/2}:1$, and, for a regular tetrahedral cluster, the three frequencies $\nu_1(a_1):\nu_2(e):\nu_3(t_2) = 2:1:2^{1/2}$.

We shall show here that metal–metal stretching modes are relatively unperturbed by other low-frequency modes such as metal–carbonyl deformations and that the metal atom polyhedron, to a good approximation, may be treated in isolation as the vibrating unit.

Experimental Section

The computer programs used in **G** matrix construction and force constant refinement were Schnachtschneider's GMAT and FPERT, respectively.[6] When the metal–metal vectors are chosen as internal coordinates, as in this work, the appropriate symmetry coordinates are often in an unfamiliar form. Symmetry coordinates for an octahedral metal cluster are therefore given in the Appendix.

Table I. Normal-Coordinate Analyses of the $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ Clusters

	$Os_3(CO)_{12}$			$Ru_3(CO)_{12}$		
mode	ν_{obsd}, cm^{-1}	ϵ,[a,4] cm^{-1}	ϵ,[a] cm^{-1}	ν_{obsd}, cm^{-1}	ϵ,[a,4] cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a_1')	158.0	1.6	5.7	185.0	−3.6	3.7
ν_2 (e')	117.0	−5.7	−7.0	149.0	5.0	−5.7
force const,						
$N\ m^{-1}$ k_r		91	106		82	83
f_{rr}		*b*	−8		*b*	−7

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$. [b] Not included in the force field.

Results and Discussion

We shall proceed by describing normal-coordinate calculations in which the metal-cluster skeleton alone is treated as the vibrating unit for some metal-cluster complexes which have been the subject of *complete* normal-coordinate analyses. The simplest metal cluster is the equilateral triangle in which three similar metal atoms are connected by metal–metal bonds alone. The best known examples of this type are $M_3(CO)_{12}$ (M = Ru, Os). Several investigations have been made into the vibrational spectra of these species; for the purposes of comparison we shall use the frequencies determined by Quicksall and Spiro.[4]

For each of these species two frequencies arise from metal–metal stretching modes, ν_1 (a_1') and ν_2 (e'), and the force field is described by two force constants, k_r, the M–M bond stretching force constant, and f_{rr}, the interaction constant between the stretching of adjacent bonds. With use of the structural parameters determined for $Os_3(CO)_{12}$[7] and $Ru_3(CO)_{12}$[8] and the metal–metal bonds as internal coordinates, the **G** matrices may be constructed. Subsequent refinement of the force constants k_r and f_{rr} yields the calculated frequencies and force constants shown in Table I, along with the corresponding data from the complete normal-coordinate analysis.[4] The agreement between observed and calculated frequencies is satisfactory in the approximate calculation, and the principal force constants compare favorably with those determined by Quicksall and Spiro.[4] It is interesting to note that a force constant calculation by Hartley, Kilty, and Ware,[9]

---

(1) T. G. Spiro, *Prog. Inorg. Chem.*, **11**, 1 (1970).
(2) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 183 (1968).
(3) V. A. Maroni and T. G. Spiro, *Inorg. Chem.*, **7**, 188 (1968).
(4) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.* **7**, 2365 (1968).
(5) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2011 (1969).
(6) J. H. Schnachtschneider, Technical Reports No. 231-64 and No. 57-65, Shell Development Co., Emeryville, CA, 1975.
(7) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).
(8) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).

0020-1669/80/1319-2825$01.00/0 © 1980 American Chemical Society

Table II. Normal-Coordinate Analyses of the $Ir_4(CO)_{12}$ Cluster

mode	ν_{obsd}, cm^{-1}	ϵ,[a, 5] cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a_1)	207.0	0.1	0.4
ν_2 (e)	131.0	0.1	−1.0
ν_3 (t_2)	161.0	−0.2	0.3
force const, N m^{-1} k_r		169	159
f_{rr}		−13	−13
$f_{rr'}$		13	13

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$.

in which $M(CO)_4$ were taken as the vibrating units, resulted in values for k_r nearly twice as great as those shown in Table I. At this point the significance of the interaction constants, f_{rr}, cannot be assessed; they might merely compensate for the exclusion of the carbonyl ligands from the calculation, or they may represent genuine interactions between the stretching of adjoining M–M bonds.

We next consider the cluster $Ir_4(CO)_{12}$, which has also been the subject of a normal-coordinate analysis.[5] The tetrahedral arrangement of the metal skeleton[10] gives rise to three fundamental metal–metal stretching modes, ν_1 (a_1), ν_2 (e) and ν_3 (t_2), and the force field requires a third force constant, $f_{rr'}$, representing interaction between the stretching of metal–metal bonds not involving a common iridium atom, in addition to the two force constants defined above. Refinement of the three force constants to reproduce the observed frequencies yields the calculated data shown in Table II. The corresponding frequency agreement and force constants calculated in the complete normal-coordinate analysis are also shown. The frequency reproduction in the present approach is very similar to that obtained previously, and excellent agreement between the two sets of force constants is also evident. It may be seen not only that the two interaction constants are identical in the two studies but also that the value of f_{rr}, determined in this work, bears approximately the same relationship to k_r as was found in the case of the $M_3(CO)_{12}$ clusters above, that is, as in eq 2. If this approximation were to be of general validity

$$f_{rr} \simeq -0.08k_r \qquad (2)$$

in the force fields of metal cluster skeletons, a significant reduction in the number of independent force constants is possible. Concerning the significance of the force constant f_{rr}, we may now, by comparison with its value in the complete normal-coordinate analysis, regard it as a genuine interaction between the stretching of metal–metal bonds within the skeleton of the cluster. More reservation must be used in assessing the significance of the interaction constant $f_{rr'}$, but in this case we note that

$$f_{rr'} \simeq -f_{rr} \simeq 0.08k_r \qquad (3)$$

These empirical relationships mean that the force field of the tetrahedral cluster is reduced to a single-parameter problem. A calculation in which the force constant $f_{rr'}$ was constrained to zero resulted in reasonable frequency reproduction which however was somewhat inferior to that obtained with the three force constants.

Metal Clusters Containing Bridging Ligands. The presence of μ- or μ_3-bridging ligands spanning metal–metal bonds in a cluster complex might be expected to modify the observed frequencies of the M–M stretching modes both as a result of the change in the effective force constant for the stretching of that bond and as a result of vibrational interaction between the M–M and symmetric M_2L stretching modes. The latter effect will be minimized when the frequency separation of these two modes is substantial, as is the case for μ-bridging hydride ligands. A simple example of this situation, analogous to the $M_3(CO)_{12}$ clusters considered above, occurs in the $Mn_3H_3(CO)_{12}$ species. The Mn–Mn stretching modes in this complex have been reported to occur at 163 (a_1') and 144 cm^{-1} (e'),[12] while the symmetric Mn_2H stretches occur near 900 cm^{-1}. Force constant refinement, with the constraint of expression 2, gives the calculated data shown in Table III. The calculated force constant for Mn–Mn stretching, k_r = 37 N m^{-1}, is very low but seems reasonable when compared with the value of 59 N m^{-1} obtained from the normal-coordinate analysis of the dimeric species $Mn_2(CO)_{10}$.[13] Also, the Mn–Mn bonds are believed to be significantly weakened by the presence of the μ-bridging hydride ligands.[14]

Table III. Approximate Normal-Coordinate Analysis of the $Mn_3H_3(CO)_{12}$ Cluster

mode	ν_{obsd}, cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a_1')	163.0	−5.9
ν_2 (e')	144.0	8.6
force const, N m^{-1} k_r		37
f_{rr}		$-0.08k_r$

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$.

Table IV. Normal-Coordinate Analyses of the $Pb_4(OH)_4^{4+}$ Cluster

mode	ν_{obsd}, cm^{-1}	ϵ,[a, 3] cm^{-1}	ϵ,[a] cm^{-1}	ϵ,[a] cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a_1)	130	5	3.6	15	0.0
ν_2 (e)	60	−5	−3.2	−13	0.1
ν_3 (t_2)	87	−3	−2.4	−2	−0.1
force const, N m^{-1} k_r		54	49	53	47
f_{rr}		b	b	$-0.08k_r$	1.3
$f_{rr'}$		b	b	$0.08k_r$	b

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$. [b] Not included in force field.

Table V. Normal-Coordinate Analyses of the $Bi_6(OH)_{12}^{6+}$ Cluster

mode	ν_{obsd}, cm^{-1}	ϵ,[a, 2] cm^{-1}	ϵ,[a] cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a_{1g})	177	1	7.7	−1.0
ν_2 (e_g)	90	2	5.3	8.5
ν_3 (t_{1u})	b	c		c
ν_4 (t_{2g})	108	−5	−11.7	−3.6
force const, N m^{-1} k_r		96	88	82
f_{rr}		d	d	3

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$. [b] Not observed. [c] Frequency of ν_3 (t_{1u}) inferred as 148[2] and 146 cm^{-1} (present work). [d] Not included in force field.

In our present approach the perturbation to the metal–metal stretching modes which may be caused by the presence of bridging ligands would be expected to be manifest as a significant deviation of the value of f_{rr} from that predicted by expression 2. To investigate this assumption we have subjected the tetrahedral, μ_3-hydroxy-bridged cluster $Pb_4(OH)_4^{4+}$[11] to an approximate normal-coordinate treatment, following the procedure outlined above for the cluster $Ir_4(CO)_{12}$. Force constant refinement to a single-parameter force field as defined by expressions 2 and 3 gives only modest reproduction of the observed frequencies (average error 10 cm^{-1}). When, however, a force field is calculated in which k_r and f_{rr} are independent, the frequency agreement is excellent (Table IV), and the value

---

(9) D. Hartley, P. A. Kilty, and M. J. Ware, *Chem. Commun.* 493 (1968).

(10) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, 1966; *Diss. Abstr.*, **26**, 5029 (1966).

(11) O. E. Esval, Thesis, University of North Carolina, 1962.

(12) M. W. Howard, Ph.D. Thesis, University of East Anglia, 1979.

(13) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **8**, 2363 (1969).

(14) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).

of the principal Pb–Pb bond stretching force constant is in quite good agreement with the value derived from a complete normal-coordinate analysis.[3] Also included in Table IV are the results of a calculation in which both f_{rr} and $f_{rr'}$ were constrained to zero. It would thus appear that, consistent with the above discussion, the presence of the μ_3-bridging hydroxyl ligands modifies the value of the interaction constant f_{rr} from ca. −8% of k_r found earlier to ca. 3%.

A more complex metal cluster which has been the subject of a normal-coordinate analysis is the octahedral species $Bi_6(OH)_{12}^{6+}$. This ion is believed to take the form of a regular octahedron of bismuth atoms with each edge being bridged by a hydroxide ligand.[15] The calculations performed on the metal framework of this cluster are summarized in Table V along with the results from the normal-coordinate analysis (in which only the hydrogen atoms were omitted).[2] In the case of this cluster our calculated value of k_r (82 N m^{-1}) differs somewhat from the normal-coordinate value (96 N m^{-1}) when the frequency agreement is roughly comparable. As was found for the $Pb_4(OH)_4^{4+}$ ion above, the interaction force constant f_{rr} is found to be ca. 3% of k_r, and the interaction constants associated with the stretching of M–M bonds not having a common atom are insignificant.

These calculations thus show that reasonable metal–metal bond stretching force constants may be derived from a consideration of the metal cluster alone and that the presence of bridging ligands of appreciable mass merely leads to a modification in the interaction force constant associated with the stretching of adjacent metal–metal bonds. The latter conclusion must be rather tentative at present since another possible cause of the variation in f_{rr} could be associated with the unusually long metal–metal bonds present in these main-group clusters (Pb–Pb = 3.81 Å, Bi–Bi = 3.71 Å).

Metal Clusters of Reduced Symmetry. We have hitherto considered metal clusters in which the maximum molecular symmetry prevails. Extension of this approach to clusters where the symmetry is lowered, for example, by asymmetric substitution, must be considered less than promising despite the simplifications made possible by the use of expression 2, where appropriate. This is due to the number of force constants increasing substantially upon symmetry lowering, compared with the number of "extra" frequencies which may be observed as a result of lifting of degeneracies and relaxing of selection rules. In order to discover to what extent this type of calculation remains feasible, we have applied it to the clusters $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$. These species differ from the $Ir_4(CO)_{12}$ cluster discussed above in that, in each case, one face of the metal atom "tetrahedron" is associated with three μ-bridging carbonyl ligands; i.e., these species are more accurately formulated as $M_4(\mu\text{-}CO)_3(CO)_9$. The molecular symmetry in the crystal, for each complex, is close to C_{3v},[15] and the vibrational spectra have been interpreted on this basis.[16-18]

The number of force constants required in the force field of the C_{3v} skeleton of the Rh complex is 6, which we designate as k_r and k_R, the principal force constants for Rh–Rh stretching, f_{rr} and f_{RR}, the interaction constants between coordinates of the same type, f_{rR}, the interaction constant between adjacent bonds of different types, and $f_{rR'}$, the interaction constant between the stretching of bonds not possessing a common Rh atom. We shall take the subscript "r" to refer to nonbridged Rh–Rh bonds and "R" to refer to those bridged by a carbonyl ligand. The number of fundamental frequencies arising from this metal skeleton is 4 (2 a$_1$ + 2 e). We reduce the number of independent force constants using expression 2, making the assumptions

$$f_{rr} = -0.08k_r \tag{4}$$

$$f_{RR} = -0.08k_R \tag{5}$$

Calculation showed that, of the remaining four independent force constants, the interaction between unconnected coordinates, $f_{rR'}$, is insignificant and that its inclusion in the force field as suggested by eq 3 leads to poor frequency reproduction. This is shown in Table VI. The force constant f_{rR}, it was found, could not be included in the force constant refinement since its unconstrained presence caused oscillations involving reversion of the values of k_r and k_R. It was thus fixed with a value of −8% of the mean Rh–Rh stretching force constant; this resulted in the calculated frequencies and force constants shown in Table VI. The reasonable agreement between observed and calculated frequencies seems to support the validity of this approach and to lend weight to the significance of the interaction constants associated with the stretching of adjacent metal–metal bonds.

Table VI. Approximate Normal-Coordinate Analysis of the $Rh_4(CO)_{12}$ Cluster

mode		ν_{obsd}, cm^{-1}	ϵ,[a] cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a$_1$)		225.0	−9.5	−3.2
ν_2 (a$_1$)		174.0	8.6	3.7
ν_3 (e)		197.0	12.9	5.3
ν_4 (e)		128.0	−7.9	−5.6
force const, N m^{-1}	k_r		80	81
	k_R		125	128
	f_{rr}		$-0.08k_r$	$-0.08k_r$
	f_{RR}		$-0.08k_R$	$-0.08k_R$
	f_{rR}		−8[b]	−8[b]
	$f_{rR'}$		8	c

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$. [b] This value of f_{rR} was chosen as −8% of the mean Rh–Rh stretching force constant and was fixed in the final stage of the refinement. [c] Not included in force field.

Table VII. Approximate Normal-Coordinate Analysis of the $Os_3(OCH_3)_2(CO)_{10}$ Cluster

mode		ν_{obsd}, cm^{-1}	ϵ,[a] cm^{-1}
ν_1 (a$_1$)		172.0	−1.0
ν_2 (a$_1$)		136.0	8.1
ν_3 (b$_2$)		119.0	−5.1
force const, N m^{-1}	k_r		101
	k_R		158
	f_{rr}		$-0.08k_r$
	f_{rR}		−10[b]

[a] $\epsilon = \nu_{obsd} - \nu_{calcd}$. [b] This value of f_{rR} was chosen as −8% of the mean Os–Os stretching force constant and was fixed in the final stage of the refinement.

Table VIII. Approximate Force Constants for Metal-Metal Bonds in Some Transition-Metal-Cluster Complexes[a, b]

complex	k_r	complex	k_r	complex	k_r
$Mn_2(CO)_{10}$	41[1]			$Co_4(CO)_{12}$	54[c]
$Mn_3H_3(CO)_{12}$	37				
$Tc_2(CO)_{10}$	61[1]	$Ru_3(CO)_{12}$	83	$Rh_4(CO)_{12}$	81[c]
$Re_2(CO)_{10}$	82[1]	$Os_3(CO)_{12}$	106	$Ir_4(CO)_{12}$	159
		$Os_3(OCH_3)_2(CO)_{10}$	101[c]		

[a] Force constants in N m^{-1}. [b] All values of k_r derived from the metal skeleton alone. [c] Value of k_r for nonbridged metal–metal bond.

A similar approach to the $Co_4(CO)_{12}$ cluster is possible. However, for this species only three of the four metal–metal

---

(15) C. H. Wei., *Inorg. Chem.*, **8**, 2384 (1969).
(16) E. W. Abel and R. A. N. McLean, *Inorg. Nucl. Chem. Lett.*, **5**, 381 (1969).
(17) F. Cariati, P. Fantucci, V. Valenti, and P. Barone, *Rend. Ist. Lomb. Accad. Sci. Lett. A*, **105**, 122 (1971).
(18) S. Onaka and D. F. Shriver, *Inorg. Chem.*, **15**, 915 (1976).

Table IX

		r_1	r_2	r_3	r_4	r_5	r_6	r_7	r_8	r_9	r_{10}	r_{11}	r_{12}	N
S_1	a_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	$12^{-1/2}$
S_2	e_g	1	1	1	1	1	1	1	1	−2	−2	−2	−2	$24^{-1/2}$
S_3		1	−1	1	−1	1	−1	1	−1	0	0	0	0	$8^{-1/2}$
S_4	t_{1u}	1	1	1	1	−1	−1	−1	−1	0	0	0	0	$8^{-1/2}$
S_5		0	1	0	−1	0	1	0	−1	−1	1	1	−1	$8^{-1/2}$
S_6		1	0	−1	0	1	0	−1	0	1	1	−1	−1	$8^{-1/2}$
S_7	t_{2g}	0	0	0	0	0	0	0	0	1	−1	1	−1	2^{-1}
S_8		1	0	−1	0	−1	0	1	0	0	0	0	0	2^{-1}
S_9		0	1	0	−1	0	−1	0	1	0	0	0	0	2^{-1}
S_{10}	t_{2u}	1	−1	1	−1	−1	1	−1	1	0	0	0	0	$8^{-1/2}$
S_{11}		0	1	0	−1	0	1	0	−1	1	−1	−1	1	$8^{-1/2}$
S_{12}		1	0	−1	0	1	0	−1	0	−1	−1	1	1	$8^{-1/2}$

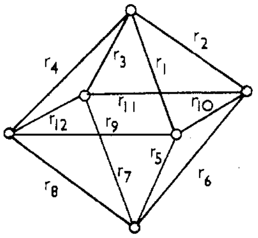


Figure 1. Internal coordinate definitions for an octahedral metal cluster.

stretching fundamentals have been identified, and the agreement between calculated and observed frequencies suffers accordingly. Values for k_r and k_R of 54 and 94 N m^{-1}, respectively, are calculated, and the frequency of the mode which has not been observed, ν_4 (e), is inferred as 140–150 cm^{-1}. A very weak absorption has been observed in the far-infrared spectrum of $Co_4(CO)_{12}$, at liquid-nitrogen temperature, at 145 cm^{-1} [19] which may arise from this mode.

As a final application of this type of calculation, we consider the triangular metal cluster $Os_3(OCH_3)_2(CO)_{10}$. X-ray diffraction studies have shown this cluster to possess a structure in which one Os–Os bond is bridged by both methoxy ligands.[20] The latter bond is approximately 0.2 Å longer than the other two metal–metal bonds, which are of almost equal length. Using the same notation as for $Rh_4(CO)_{12}$ above, we have four force constants, k_r, k_R, f_{rr}, and f_{rR}, and three frequencies. Use of expression 2 and refinement of the two independent force constants (f_{rR} was constrained in a similar way to the method used for $Rh_4(CO)_{12}$) to reproduce the observed frequencies[9] lead to the calculated data shown in Table VII. The value of k_r, the force constant associated with stretching of the unbridged Os–Os bonds, is very close to that calculated in the equilateral triangular cluster $Os_3(CO)_{12}$ above, while it would appear that the two μ-methoxy groups raise the force constant for stretching of the bridged Os–Os bond by ca. 50%.

Force Constants of Metal–Metal Bonds in Metal-Cluster Complexes. We have seen here that, in cases where complete normal-coordinate analyses have been carried out previously, the force constants calculated for metal–metal bond stretching in the metal polyhedra alone compare quite well with those determined by the more rigorous method. This may very well not be the case when heavier substituents are attached to the metal atoms (for example, sulfur or phosphorus ligands), and this approach might even be rendered invalid by the presence of ligands such as μ_3-bridging CO, where the symmetric M_2C stretching modes are relatively close to the metal–metal stretches. These qualifications notwithstanding, the approximate force field afforded by the use of the metal atom framework alone appears to give encouraging results which might be expected to reveal trends in the force constants of metal–metal bonds. We have tabulated, in Table VIII, M–M bond stretching force constants for transition-metal clusters. These data are all derived from calculations in which first-row ligands have been ignored (denoted by "NFRL" in Spiro's review[1]). A rather satisfactory trend is apparent with k_r increasing with atomic number, both within a given row and on passing to succeeding rows. The data derived in the present work thus provide support for Spiro's earlier suggestion that such a trend, in fact, exists.[1]

General Discussion. This paper has described the application of approximate normal-coordinate methods to the vibrational frequencies of metal–metal bonds in metal-cluster complexes with the assumption that these vibrational modes may be treated as arising from the metal atom skeleton alone. The analysis permitted the calculation of frequencies which are in good agreement with those observed. In addition, the calculated principal force constants for M–M bond stretching are in fair agreement with those available from complete normal-coordinate analyses. The approximate force field used in these calculations contained an interaction force constant associated with the stretching of adjacent metal–metal bonds. This force constant has been found to be significant in each calculation undertaken and has been shown empirically to assume a value of ca. −8% of the principal force constant for transition-metal clusters and ca. 3% of k_r in clusters of main-group metals. It is not known whether this difference arises from the presence of bridging hydroxyl ligands or is a consequence of the long, weak metal–metal bonds present in the latter clusters. The second of these possibilities may be somewhat more likely in view of the observation that, for some transition-metal clusters considered here, the relative magnitude of the interaction force constant is unaffected by the presence of bridging carbonyl or methoxide ligands (cf. $Rh_4(CO)_{12}$ and $Os_3(OCH_3)_2(CO)_{10}$ above).

The interaction force constant associated with the stretching of bonds not possessing a common metal atom was found to be insignificant in the larger metal clusters investigated, with the exception of $Ir_4(CO)_{12}$. Its significance in the force field of this cluster may be due to the rather large value of the principal force constant in this case (159 N m^{-1}).

The approximate force field developed in this paper appears to offer a straightforward method for extracting meaningful metal–metal bond stretching force constants from the observed metal–metal stretching frequencies of cluster complexes. Its applicability to larger metal clusters cannot be assessed until vibrational data for such complexes become available.

Acknowledgment. The author is indebted to Professors S. F. A. Kettle and N. Sheppard and Drs. J. L. Duncan and D. B. Powell for helpful discussions.

Appendix

Symmetry Coordinates in Metal Atom Polyhedra. Throughout this work internal coordinates have been chosen

---

(19) J. R. Andrews, Ph.D. Thesis, University of East Anglia, 1979.

(20) V. F. Allen, R. Mason, and P. B. Hitchcock, *J. Organomet. Chem.*, **140**, 297 (1977).

to coincide with the metal–metal vectors. Those appropriate to the tetrahedron were identical with the set used in the normal-coordinate analysis of the P_4 molecule.[21] We give here (Table IX) symmetry coordinates for an octahedral cluster; internal coordinates are defined in Figure 1.

Registry No. $Os_3(CO)_{12}$, 15696-40-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ir_4(CO)_{12}$, 18827-81-1; $Mn_3H_3(CO)_{12}$, 51160-01-1; $Pb_4(OH)_4^{4+}$, 31387-73-2; $Bi_6(OH)_{12}^{6+}$, 12441-70-2; $Rh_4(CO)_{12}$, 19584-30-6; $Os_3(OCH_3)_2(CO)_{10}$, 41766-82-9; $Co_4(CO)_{12}$, 17786-31-1.

---

[21] C. W. F. T. Pistorius, *J. Chem. Phys.*, **29**, 1421 (1958).

Notes

Contribution from the Chemistry Division,
Naval Research Laboratory, Washington, D.C. 20375, and the
Department of Chemistry, Georgetown University,
Washington, D.C. 20057

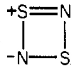
The X-ray Photoelectron Spectrum of S_2N_2 Gas

Patrick Brant,*[1a] David C. Weber,[1a] Curtis T. Ewing,[1a]
Forrest L. Carter,[1a] and Joseph A. Hashmall[1b]

Received October 16, 1979

S_2N_2 is a square molecule (D_{2h} symmetry)[2] formed from the interaction of S_4N_4 vapor with silver wool at 150 °C. On warming, condensed S_2N_2 undergoes polymerization (0 °C) to the conducting polymer $(SN)_x$ (polythiazyl).[2,3] Largely as a consequence of the relationship of S_2N_2 with $(SN)_x$ the bonding and charge distribution in S_2N_2 have been a matter of considerable speculation.[4] The bonding in S_2N_2 can formally be represented by valence bond structures I and II.


I


II

These valence bond (VB) structures suggest an S–N bond order of between 1.25 and 1.50 and *formal* S→N charge transfer of between 0 and 0.5 e. Within the valence bond formalism, decreasing S→N charge transfer requires N(pπ)→S(dπ) back-bonding (VB structure II). The extent of participation of sulfur 3d orbitals in the bonding of sulfur compounds has been a controversial issue for several years now.[5a,b] Jolly and co-workers[5c] have utilized X-ray photoelectron spectroscopy (XPS) to evaluate the contribution of sulfur 3d orbitals to the bonding of a variety of sulfur compounds and found that the XPS data could be very satisfactorily explained without the inclusion of S 3d orbitals. In an effort to estimate the charge distribution and extent of S 3d orbital participation in the bonding of S_2N_2, we have obtained core-level binding energies for gaseous S_2N_2 using XPS. The results have been interpreted with the aid of CHELEQ (electronegativity equalization)[5d] and semiempirical MNDO[6] MO calculations.

Table I. Core Level Data for S_2N_2 from X-ray Photoelectron Spectroscopy

	S $2p_{1/2}$	S $2p_{3/2}$	S 2s	N 1s
binding energy, eV[a]	173.64 (10)[c]	172.44 (10)	236.58 (5)	405.86 (5)
FWHM[b]	1.09	1.08	2.15	1.09

[a] Binding energies standardized to a value of 248.62 eV for the Ar $2p_{3/2}$ level of argon gas. [b] Peak full widths at half maxima (FWHM), in eV. [c] Estimated standard deviations (3σ) are given in parentheses.

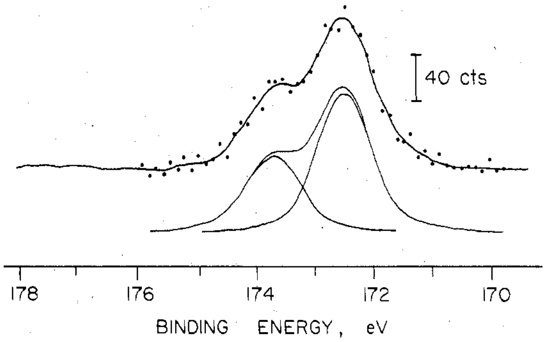


Figure 1. S $2p_{1/2}$, $2p_{3/2}$ spectrum of S_2N_2 gas and the simulated spectrum showing the curve-resolved $2p_{1/2}$ and $2p_{3/2}$ components. The components have 50:50 Gaussian–Lorentzian line shapes.

Experimental Section

S_2N_2 was freshly prepared according to the established procedure.[2] Spectra were recorded with a McPherson ESCA-36 photoelectron spectrometer equipped with a Mg Kα (1253.6 eV) X-ray source. The McPherson gas sample cell was fitted with indium gaskets and a 1-mil aluminum window to isolate the sample from the X-ray source. Pressures in the sample chamber ranged from high 10^{-7} to low 10^{-6} torr during data collection. The S_2N_2 was introduced into the gas cell via an evacuated glass vessel. Sufficient S_2N_2 pressure for data collection was maintained by *gently* warming the glass vessel (ca. ≤ 40 °C) with a hot air blower.

Data were collected and processed with a PDP-12 computer. Curve resolution of the S $2p_{1/2}$ and $2p_{3/2}$ levels was achieved by using a Gaussian–Lorentzian curve generation subroutine which is part of the McPherson program package. The simulated and experimental curves were judged equivalent by visual comparison of the curves. Core-level binding energies were standardized to the Ar $2p_{3/2}$ level of argon gas (248.62 eV),[7] spectra of which were recorded immediately before and after data collection for S_2N_2. The two Ar $2p_{3/2}$ binding energies recorded were identical within experimental error.

MNDO calculations on S_2N_2 were performed on the IBM 370/145 computer at Georgetown University using QCPE program no. 353. All geometry parameters were optimized. CHELEQ calculations were performed on the Texas Instruments Advanced Scientific Computer

---

(1) (a) Naval Research Laboratory. (b) Georgetown University.
(2) Milkulski, C. M.; Russo, P. J.; Saran, M. S.; MacDiarmid, A. G.; Garito, A. F.; Heeger, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6358.
(3) (a) Walatka, V. V.; Labes, M. M.; Perlstein, J. H. *Phys. Rev. Lett.* **1973**, *31*, 1139. (b) Greene, R. S.; Grant, P. M.; Street, G. B. *Ibid.* **1975**, *34*, 89.
(4) (a) Salahub, D. R.; Messmer, R. P. *J. Chem. Phys.* **1976**, *64*, 2039. (b) Yamabe, J.; Tanaka, K.; Fukui, K.; Kato, H. *J. Phys. Chem.* **1977**, *81*, 727. (c) Salaneck, W. R.; Lin, J. W.-p.; Paton, A.; Duke, C. B.; Ceasar, G. P. *Phys. Rev. B: Solid State* **1976**, *13*, 4517. (d) Tanaka, K.; Yamabe, J.; Tachibana, A.; Kato, H.; Kenichi, F. *J. Phys. Chem.* **1978**, *82*, 2121. (e) Findlay, R. H.; Palmer, M. H.; Downs, A. J.; Edgell, R. G.; Evans, R. *Inorg. Chem.*, in press.
(5) (a) Gleiter, R. *J. Chem. Soc. A* **1970**, 3174. (b) Noodleman, L.; Mitchell, K. A. R. *Inorg. Chem.* **1978**, *17*, 2710. (c) Jolly, W. L.; Lazarus, M. S.; Glemser, O. *Z. Anorg. Allg. Chem.* **1974**, *406*, 209. (d) Jolly, W. L.; Perry, W. B. *J. Am. Chem. Soc.* **1973**, *95*, 5442.
(6) Dewar, M. J. S.; Thiel, N. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(7) Johansson, G.; Hedman, J.; Berndstsson, A.; Klasson, M.; Nilsson, R. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 295.