volume of ice-cold CCl_4 to extract most of the XeF_2.[2] The aqueous phase was removed and the bulk of the CCl_4 was transferred to another vessel and centrifuged. An aliquot of the centrifuged CCl_4 was then shaken with aqueous 0.2 M NaOH to back-extract and decompose the XeF_2. This NaOH solution was counted, and its fluoride content was determined. Less than 0.004% of the total activity remained in the CCl_4 after back-extraction.

"Blank" experiments were carried out in the same way, but with no XeF_2 present. In such experiments less than 0.002% of the total activity was extracted into the CCl_4 and back-extracted with NaOH.

Results

A saturated XeF_2 solution at 0° was found to have a specific conductance of 4×10^{-4} (ohm cm)$^{-1}$. A 4.2×10^{-3} M solution of HF at 0° was found to have closely the same specific conductance.

Two reaction mixtures were typical of the fluorine exchange experiments. One contained 0.14 M XeF_2 and 0.33 M HF*; the other contained 0.13 M XeF_2, 0.13 M HF*, and 0.18 M KF*. In each of these experiments 25 ± 0.5% of the total fluorine was obtained by extracting the XeF_2 into CCl_4 and back-extracting it with base. In each case this fluorine contained 0.21 ± 0.01% of the total F^{18} activity. Thus after 2 hr at 0°, exchange had proceeded only to the extent of about 0.8%.

Discussion

The conductance found for a saturated XeF_2 solution is probably that of HF formed in the oxidation of water by XeF_2[2]

$$XeF_2 + H_2O \longrightarrow Xe + {}^1/_2O_2 + 2HF \qquad (1)$$

This reaction has a half-time at 0° of about 7 hr.[2] Among other reactions that might contribute to the condutance are

$$XeF_2 + H_2O \longrightarrow XeF(OH) + HF \qquad (2)$$

and

$$XeF_2 \longrightarrow XeF^+ + F^- \qquad (3)$$

If either of these reactions proceeded to the extent of about 3%, it could account for the entire observed conductance. Any other reaction one might write would have to produce at least as much conductance if it proceeded to the same extent. Hence, we can say, in any case, that at least 97% of the xenon difluoride dissolved in water is initially present in solution as molecular XeF_2.

The observed fluoride exchange between XeF_2 and aqueous fluoride is so slow that we may rule out the occurrence of any *reversible* reactions similar to reactions 2 and 3. We may also exclude such equilibria as

$$XeF_2 + 2F^- \rightleftarrows XeF_4{}^{2-} \qquad (4)$$

in which the fluorine atoms in the complex ion are equivalent.

Acknowledgments.—We wish to thank Mrs. Alberta Martin and Mrs. Emily White for extensive technical assistance.

Correspondence

Force Constants for CO Bonds in Metal Carbonyls[1]

Sir:

There have been reported[2-6] a number of treatments of metal carbonyls in which the CO stretching force constants and CO,CO interaction constants have been calculated with neglect of all other force constants in the molecule. This gross approximation has apparently proved useful in making frequency assignments. However, little indication has been given as to how these "approximate" force constants may differ from the true harmonic force constants in a general quadratic valence force field.[7,8] For this reason it seems appropriate to compare the results obtained using the approximate method with those obtained using a more rigorous treatment for a given molecule. The hexacarbonyl of molybdenum is a well-studied example.

Recently[8] anharmonic corrections and harmonic frequencies were determined for the hexacarbonyls of Cr, Mo, and W. The harmonic frequencies are the appropriate values to use for force constant calculations, and the results calculated therefrom must be considered the most accurate. We shall compare the harmonic with the uncorrected results, as well as comparing the rigorous and "approximate" methods. The equations for the more rigorous treatment are in the literature.[9] For the approximate treatment[10] of octahedral $M(CO)_6$ these reduce to

---

(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) (a) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); (b) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(3) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(4) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *ibid.*, **3**, 1123 (1964).

(5) D. K. Huggins, N. Flitcroft, and H. D. Kaesz, *ibid.*, **4**, 166 (1965).

(6) G. R. Van Hecke and W. D. Horrocks, Jr., *ibid.*, **5**, 1960 (1966).

(7) Van Hecke and Horrocks[6] did compare "approximate" calculations with "rigorous" calculations for $Co(NO)(CO)_3$, $Ni(CO)_4$, and $Mo(CO)_6$. However, harmonic frequencies (corrected for anharmonicity) were not available for the first molecule, and considerable revision[8] is necessary for the anharmonic corrections of the last two.

(8) J. M. Smith and L. H. Jones, *J. Mol. Spectry.*, **20**, 248 (1966).

(9) L. H. Jones, *ibid.*, **8**, 105 (1962).

(10) The approximate treatment referred to entails the neglect of all force constants but F_{CO}, $F_{CO,CO'}$, and $F_{CO,CO''}$; that is, $F_{MC,CO} = 0$, $F_{MC,CO'} = 0$, $F_{MC,CO''} = 0$, $F_{MC} = 0$, $F_{MC,MC'} = 0$, $F_{MC,MC''} = 0$, etc. Cotton and Kraihanzel[2] made the further approximation that $F_{CO,CO'} = 2F_{CO,CO''}$ This is not assumed here.

TABLE I

CO STRETCHING FORCE CONSTANTS[a] OF $Mo(CO)_6$ IN CCl_4 SOLUTION

	Assumed[b]			Harmonic[c]			Anharmonic[c]		
No.	$F_{MC,CO}$	$F_{MC,CO''}$	$F_{MC,CO'}$	F_{CO}	$F_{CO,CO''}$	$F_{CO,CO'}$	F_{CO}	$F_{CO,CO''}$	$F_{CO,CO'}$
1	0	0	0	16.29	0.28	0.15	15.75	0.27	0.35
2	0.5	0	0	16.90	0.28	0.16	16.36	0.27	0.35
3	0.5	0	−0.125	16.88	0.28	0.02	16.36	0.27	0.20
4	0.5	−0.125	0	16.90	0.13	0.16	16.36	0.11	0.35
5	0.5	−0.125	−0.125	16.88	0.13	0.02	16.36	0.11	0.20
6	All $F_{ij} = 0$ except F_{CO}, $F_{CO,CO''}$, and $F_{CO,CO'}$			17.00	0.29	0.36	16.46	0.27	0.55

[a] All force constants are in units of millidynes per Ångstrom. [b] $F_{MC,CO}$ is for interaction of an MC bond with a CO bond involving the same C atom. $F_{MC,CO''}$ is for interaction at 90° and $F_{MC,CO'}$ at 180°. [c] The harmonic frequencies (cm^{-1}) are $\omega_1 = 2141$, $\omega_2 = 400$, $\omega_3 = 2038$, $\omega_4 = 390$, $\omega_6 = 2030$, $\omega_7 = 593$, $\omega_8 = 367$, and $\omega_9 = 91$. For the anharmonic frequencies $\nu_1 = 2117$, $\nu_3 = 2019$, and $\nu_6 = 1985$; the other ν_i remain the same.

$$F_{11}^{A_{1g}} = F_{CO} + 4F_{CO,CO''} + F_{CO,CO'} = \lambda_1/(\mu_C + \mu_O)$$

$$F_{33}^{E_g} = F_{CO} - 2F_{CO,CO''} + F_{CO,CO'} = \lambda_3/(\mu_C + \mu_O)$$

$$F_{66}^{F_{1u}} = F_{CO} - F_{CO,CO'} = \lambda_6/(\mu_C + \mu_O)$$

$F_{CO,CO''}$ is for interaction at 90°; $F_{CO,CO'}$, at 180°. $\lambda_i = 4\pi^2\nu_i^2$ and μ_i is the reciprocal of mass of atom i.

For the approximate treatment the solution is unique. For the complete quadratic solution one must make assumptions about certain of the interaction constants. For this purpose we have made several choices for the MC,CO interactions and neglected the stretch–bend and bend–bend interactions. The latter two interactions, unless quite large, are found to have negligible effect on the CO force constant and CO,CO interaction constants. In Table I, harmonic and anharmonic solutions for F_{CO}, $F_{CO,CO''}$, and $F_{CO,CO'}$ are given for the various assumptions about the other force constants.[11–16] The observed frequencies, from ref 8, are given also.

There are two important facts to note. (1) Using the harmonic frequencies[17] one calculates a considerably smaller opposite bond interaction, $F_{CO,CO'}$, than if anharmonic frequencies are used; in fact, $F_{CO,CO'}$ is less than $F_{CO,CO''}$ for all reasonable MC,CO interactions, contrary to previous predictions[2a,9] and calculations.[13] (2) Neglect of the MC stretching force constant, as in the "approximate" treatment, leads to significantly different calculated CO,CO interactions, even when MC,CO interactions are neglected.

The importance of this correspondence is to point out that the "approximate" force constant calculation can be very misleading as to the absolute and relative magnitudes of the CO,CO interaction constants of metal carbonyls. Furthermore, even the rigorous method is misleading in this respect if harmonic frequencies are not used. Therefore, it is not appropriate to speculate on the significance of the interaction constants calculated by the "approximate" method. The "approximate" primary CO stretching force constants are in the right ball park and certainly trends among similar compounds (such as $M(CO)_5L$ and $M(CO)_5L'$) are meaningful. However, one should not attach much significance to slight differences in the "approximate" F_{CO} calculated for carbonyls of different symmetry, such as $M(CO)_6$ and $M(CO)_5L$. Careful studies of isotopically enriched species are required for more definitive results.

UNIVERSITY OF CALIFORNIA
LOS ALAMOS SCIENTIFIC LABORATORY
LOS ALAMOS, NEW MEXICO 87544

LLEWELLYN H. JONES

RECEIVED JANUARY 16, 1967

---

(11) We cannot at present say with certainty what the most reasonable values are for the MC,CO interaction constants. From studies on $Ni(^{13}CO)_4$[12] it appears that the primary interaction constant, $F_{MC,CO}$, should be about 0.4–0.5 mdyne/A. The constants $F_{MC,CO''}$ and $F_{MC,CO'}$ we expect[1,13] to be negative and considerably smaller than $F_{MC,CO}$. The analogous terms in metal cyanide complexes[14,15] are close to zero. Furthermore, $F_{MC,CO''}$ is expected[9] to be smaller than $F_{MC,CO'}$. Thus, at present, harmonic solution no. 2 or 3 in Table I might be considered the most reasonable.

(12) Unpublished work in this laboratory.

(13) L. H. Jones, *Spectrochim. Acta*, **19**, 329 (1963).

(14) L. H. Jones, *J. Chem. Phys.*, **43**, 594 (1965).

(15) L. H. Jones, *ibid.*, **44**, 3643 (1966).

(16) The results in Table I, as well as consideration of the secular equations, lead to the following approximate relations for the harmonic force constants of $Mo(CO)_6$: $F_{CO} \approx 16.29 + 1.2F_{MC,CO}$; $F_{CO,CO''} = 0.28 + 1.2F_{MC,CO''}$; $F_{CO,CO'} \approx 0.16 + 1.2F_{MC,CO'}$. Thus one can readily estimate the CO force constants for a given choice of MC,CO interaction constants. Similar expressions can be derived for the anharmonic force constants.

(17) It is difficult to estimate the accuracy of the harmonic frequencies; they may certainly be off by a few wavenumbers because of possible Fermi resonances and other effects. If we say the limits of error are ±5 cm^{-1} for ω_1, ω_3, and ω_6, we find the following error limits (mdyne/A) for the calculated force constants in rows 4, 5, and 6 of Table I: F_{CO}, ±0.27; $F_{CO,CO''}$, ±0.03; $F_{CO,CO'}$ ±0.11. Thus, an uncertainty of 5 cm^{-1} in the harmonic CO stretching frequencies has a significant effect on the calculated values of F_{CO} and $F_{CO,CO'}$.