

volume of ice-cold  $\text{CCl}_4$  to extract most of the  $\text{XeF}_2$ .<sup>2</sup> The aqueous phase was removed and the bulk of the  $\text{CCl}_4$  was transferred to another vessel and centrifuged. An aliquot of the centrifuged  $\text{CCl}_4$  was then shaken with aqueous 0.2  $M$   $\text{NaOH}$  to back-extract and decompose the  $\text{XeF}_2$ . This  $\text{NaOH}$  solution was counted, and its fluoride content was determined. Less than 0.004% of the total activity remained in the  $\text{CCl}_4$  after back-extraction.

"Blank" experiments were carried out in the same way, but with no  $\text{XeF}_2$  present. In such experiments less than 0.002% of the total activity was extracted into the  $\text{CCl}_4$  and back-extracted with  $\text{NaOH}$ .

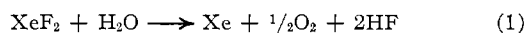
### Results

A saturated  $\text{XeF}_2$  solution at  $0^\circ$  was found to have a specific conductance of  $4 \times 10^{-4}$  (ohm cm)<sup>-1</sup>. A  $4.2 \times 10^{-3}$   $M$  solution of  $\text{HF}$  at  $0^\circ$  was found to have closely the same specific conductance.

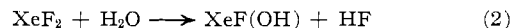
Two reaction mixtures were typical of the fluorine exchange experiments. One contained 0.14  $M$   $\text{XeF}_2$  and 0.33  $M$   $\text{HF}^*$ ; the other contained 0.13  $M$   $\text{XeF}_2$ , 0.13  $M$   $\text{HF}^*$ , and 0.18  $M$   $\text{KF}^*$ . In each of these experiments  $25 \pm 0.5\%$  of the total fluorine was obtained by extracting the  $\text{XeF}_2$  into  $\text{CCl}_4$  and back-extracting it with base. In each case this fluorine contained  $0.21 \pm 0.01\%$  of the total  $\text{F}^{18}$  activity. Thus after 2 hr at  $0^\circ$ , exchange had proceeded only to the extent of about 0.8%.

### Discussion

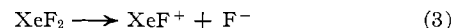
The conductance found for a saturated  $\text{XeF}_2$  solution is probably that of  $\text{HF}$  formed in the oxidation of water by  $\text{XeF}_2$ .<sup>2</sup>



This reaction has a half-time at  $0^\circ$  of about 7 hr.<sup>2</sup> Among other reactions that might contribute to the conductance are

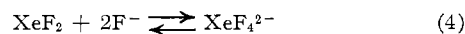


and



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  $\text{XeF}_2$ .

The observed fluoride exchange between  $\text{XeF}_2$  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



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<sup>1</sup>

Sir:

There have been reported<sup>2-6</sup> 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.<sup>7,8</sup> 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<sup>8</sup> 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.<sup>9</sup> For the approximate treatment<sup>10</sup> of octahedral  $\text{M}(\text{CO})_6$  these reduce to

(7) Van Hecke and Horrocks<sup>6</sup> did compare "approximate" calculations with "rigorous" calculations for  $\text{Co}(\text{NO})(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ , and  $\text{Mo}(\text{CO})_6$ . However, harmonic frequencies (corrected for anharmonicity) were not available for the first molecule, and considerable revision<sup>8</sup> 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  $F_{\text{CO}}$ ,  $F_{\text{CO},\text{CO}'}$ , and  $F_{\text{CO},\text{CO}''}$ ; that is,  $F_{\text{MC},\text{CO}} = 0$ ,  $F_{\text{MC},\text{CO}'} = 0$ ,  $F_{\text{MC},\text{CO}''} = 0$ ,  $F_{\text{MC}} = 0$ ,  $F_{\text{MC},\text{MC}'} = 0$ ,  $F_{\text{MC},\text{MC}''} = 0$ , etc. Cotton and Kraihanzel<sup>2</sup> made the further approximation that  $F_{\text{CO},\text{CO}'} = 2F_{\text{CO},\text{CO}''}$ . This is not assumed here.

(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).

TABLE I  
 CO STRETCHING FORCE CONSTANTS<sup>a</sup> OF Mo(CO)<sub>6</sub> IN CCl<sub>4</sub> SOLUTION

No.	Assumed <sup>b</sup>			Harmonic <sup>c</sup>			Anharmonic <sup>c</sup>		
	$F_{MC,CO}$	$F_{MC,CO''}$	$F_{MC,CO'}$	$F_{CO}$	$F_{CO,CO''}$	$F_{CO,CO'}$	$F_{CO}$	$F_{CO,CO''}$	$F_{CO,CO'}$
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

<sup>a</sup> All force constants are in units of millidynes per Ångström. <sup>b</sup>  $F_{MC,CO}$  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°. <sup>c</sup> The harmonic frequencies (cm<sup>-1</sup>) are  $\omega_1 = 2141$ ,  $\omega_2 = 400$ ,  $\omega_3 = 2038$ ,  $\omega_4 = 390$ ,  $\omega_5 = 2030$ ,  $\omega_7 = 593$ ,  $\omega_8 = 367$ , and  $\omega_9 = 91$ . For the anharmonic frequencies  $\nu_1 = 2117$ ,  $\nu_3 = 2019$ , and  $\nu_6 = 1985$ ; the other  $\nu_i$  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  $\mu_i$  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.<sup>11-16</sup> The observed frequencies, from ref 8, are given also.

There are two important facts to note. (1) Using the harmonic frequencies<sup>17</sup> one calculates a consider-

ably 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<sup>2a,9</sup> and calculations.<sup>13</sup> (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)<sub>5</sub>L and M(CO)<sub>5</sub>L') 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)<sub>6</sub> and M(CO)<sub>5</sub>L. Careful studies of isotopically enriched species are required for more definitive results.

(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  $\pm 5$  cm<sup>-1</sup> for  $\omega_1$ ,  $\omega_3$ , and  $\omega_6$ , we find the following error limits (mdyne/Å) for the calculated force constants in rows 4, 5, and 6 of Table I:  $F_{CO}$ ,  $\pm 0.27$ ;  $F_{CO,CO''}$ ,  $\pm 0.03$ ;  $F_{CO,CO'}$ ,  $\pm 0.11$ . Thus, an uncertainty of 5 cm<sup>-1</sup> in the harmonic CO stretching frequencies has a significant effect on the calculated values of  $F_{CO}$  and  $F_{CO,CO'}$ .

(11) We cannot at present say with certainty what the most reasonable values are for the MC,CO interaction constants. From studies on Ni(<sup>13</sup>CO)<sub>4</sub><sup>12</sup> it appears that the primary interaction constant,  $F_{MC,CO}$ , should be about 0.4-0.5 mdyne/Å. The constants  $F_{MC,CO''}$  and  $F_{MC,CO'}$  we expect<sup>11,13</sup> to be negative and considerably smaller than  $F_{MC,CO}$ . The analogous terms in metal cyanide complexes<sup>14,15</sup> are close to zero. Furthermore,  $F_{MC,CO''}$  is expected<sup>9</sup> 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)<sub>6</sub>:  $F_{CO} \approx 16.29 + 1.2F_{MC,CO}$ ;  $F_{CO,CO''} = 0.28 + 1.2F_{MC,CO''}$ ;  $F_{CO,CO'} \approx 0.16 + 1.2F_{MC,CO'}$ . 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.

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