Force Constants in the Hexacarbonylrhenium(I) Cation

By E. W. ABEL,* R. A. N. MCLEAN, M. G. NORTON, and S. P. TYFIELD

(*Department of Inorganic Chemistry, The University, Bristol*)

NORMAL-CO-ORDINATE analyses[1–3] of the hexacarbonyls of chromium, molybdenum, and tungsten have recently been invalidated by the reassignment[4] of several fundamentals and the allowance for anharmonicity. In a preliminary account, using the new assignments and harmonic corrections for $Mo(CO)_6$, a force field with eight force constants has been used to assess[5] energy factoring and anharmonicity in the carbonyl-stretching region.

A study of the i.r. and Raman spectra of the hexacarbonylrhenium(I) cation in $[Re(CO)_6]ClO_4$ and $[Re(CO)_6]AsF_6$ enabled us to assign[6] twelve of the thirteen fundamental frequencies. A full normal co-ordinate analysis has been undertaken for $[Re(CO)_6]^+$, and more rigorous force constants calculated. An examination of previously used force fields[2,3,7] showed the most promising[7] to be inapplicable to both $[Re(CO)_6]^+$, and the new assignments[4,6] of the neutral hexacarbonyls. Best results are obtained using a modified valence force field which employs the twelve force constants enumerated below. The calculated[6] frequencies ν_1—ν_{13} are respectively 2224, 444, 2139, 430, 354, 2131, 583, 356, 77, 486, 88, 522, and 65 cm.$^{-1}$. These have all converged precisely upon the observed frequencies (ν_1, ν_3, and ν_6 corrected for anharmonicity) with the exception of ν_9 and ν_{11} (observed at 80 and 82 cm.$^{-1}$ respectively), and the unobserved ν_{13}. The values of the selected force constants producing such a convergence are (in mdynes/Å and in the notation of ref. 7), F_{CO}, 18·304; F_{MC}, 2·759; $F'_{CO,CO}$, 0·168; $F''_{CO,CO}$, 0·238; $F'_{MC,MC}$, 0·455; $F''_{MC,MC}$, 0·035; F_{β}, 0·263; F_{α}, 0·049; $F'_{\beta,\beta}$, 0·055; $F''_{\beta,\beta}$, 0·026; $F_{MC,\beta}$, 0·145. The value of $F'_{MC,CO}$ was constrained[5] at 0·500, and the introduction of nonzero values of $F''_{MC,CO}$ and $F'''_{MC,CO}$ cause divergence in the computation of frequencies.

The ready convergence in our calculations confirms the Smith–Jones re-assignment[4] for the $M(CO)_6$ system. Whilst we find the T_{1u} δ(MCO) band is at higher energy than the T_{1u} ν(MC) bond, as previously assigned[1–3] in the $M(CO)_6$ systems, on the basis that all δ(MCO) vibrations occur at higher energy than the ν(MC) modes; our present assignment shows the T_{1g} δ(MCO) band occurring well down in the so-called ν(MC) region of 500—350 cm.$^{-1}$. Thus a generalized energy separation[8] of ν(MC) and δ(MCO) modes is invalid and a reassessment of many earlier assignments[9] of substituted octahedral metal carbonyls may be necessary.

Based on π-bonding considerations,[10] the rhenium–carbon bond in $Re(CO)_6^+$ should be weaker than the tungsten–carbon bond in isoelectronic $W(CO)_6$. Using our same force field we find the M–C force constants in $Re(CO)_6^+$ and $W(CO)_6$ are Re–C 2·76 and W–C 2·73 mdynes/Å. It would therefore, appear that the overall effect of the formal positive charge has virtually no effect on the strength of the metal–carbon bond; any loss in π-bonding is presumably compensated by improved σ-donation.

In line with previous criticisms[5,11,12] of the approximate method of calculation of CO force constants in octahedral species, we find that the ratio (0·7) of *trans* : *cis* CO interaction constants in $Re(CO)_6^+$ is very different from the predicted value of 2 in these approximations[7,13] and that harmonized CO frequencies produce significantly greater values of CO force constants.[5]

The use of these harmonic frequencies for the CO-stretching modes has been shown[5] to be essential for the calculation of meaningful force constants. However, even with the use of harmonic CO frequencies to determine the CO force constant in $Re(CO)_6^+$, the rigorous value (18·30 mdynes/Å) and the approximate value (18·67 mdynes/Å) are still significantly different. This difference is a consequence of the approximations in energy factoring; thus for $Re(CO)_6^+$ our calculation of potential-energy distribution shows that 6% of the energy in the CO-stretching frequencies is accounted for by mixing with lower-energy vibrations. This shows that energy factoring can change CO-stretching force constants appreciably, though the degree of change could be similar within a particular symmetry class, such as the much studied $M(CO)_5X$ types.[14]

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[1] H. Murata and K. Kawai (*a*) *J. Chem. Phys.*, 1957, **27**, 605; (*b*) *Bull. Chem. Soc. Japan*, 1960, **33**, 1008; C. W. F. T. Pistorius and P. C. Haarhoff, *J. Mol. Spectroscopy*, 1958, **28**, 736.

[2] L. H. Jones, *Spectrochim. Acta*, 1963, **19**, 329.

[3] J. Brunvoll and S. J. Cyvin, *Acta Chem. Scand.*, 1964, **18**, 1417.

[4] J. M. Smith and L. H. Jones, *J. Mol. Spectroscopy*, 1966, **20**, 248.

[5] L. H. Jones, *Inorg. Chem.*, 1967, **6**, 1269.

[6] E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, in the press.

[7] L. H. Jones, *J. Mol. Spectroscopy*, 1962, **8**, 105.

[8] D. M. Adams, "Metal Ligand Vibrations," Edward Arnold, London, 1967, p. 118.

[9] R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301; D. M. Adams, *J. Chem. Soc.*, 1964, 1771; M. A. Bennett and R. J. H. Clark, *ibid.*, p. 5560; D. A. Brown and D. G. Carroll, *ibid.*, 1965, 2822; R. W. Cattrall and R. J. H. Clark, *J. Organometallic Chem.*, 1966, **6**, 167; A. A. Chalmers, J. Lewis, and R. Whyman, *J. Chem. Soc.* (*A*), 1967, 1817; E. Lindner and H. Behrens, *Spectrochim. Acta*, 1967, **23***A*, 3025; I. J. Hyams, D. Jones, and E. R. Lippincott, *J. Chem. Soc.* (*A*), 1967, 1987.

[10] E. W. Abel, *Quart. Rev.*, 1963, **17**, 133.

[11] L. M. Bower and M. H. B. Stiddard, *Inorg. Chim. Acta*, 1967, **1**, 231 and references therein.

[12] A. Loutellier and M. Bigorgne, *Bull. Soc. chim. France*, 1965, 3186.

[13] F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

[14] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, 1967, **89**, 2844; F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, 1967, **6**, 1357; B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc.* (*A*), 1968, 522.