

SHORT COMMUNICATIONS

POTENTIAL CONSTANTS FOR THE HEXAFLUORIDES OF MOLYBDENUM AND RHENIUM*

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The vibrational spectra of molybdenum hexafluoride and rhenium hexafluoride were first studied by Gaunt^{1, 2} and Burke, Smith, and Nielsen.³ On the basis of the fundamental frequencies assigned by these authors, the calculations of potential constants, thermodynamic functions, and mean amplitudes of vibration were carried out by Venkateswarlu and Sundaram,⁴ Pistorius,⁵ Nagarajan,⁶⁻⁸ and Sundaram.⁹ But the bending vibration ν_4 coming under the symmetry species F_{1u} was not correctly assigned by the previous workers due to the impurity for both molecules. Recently Claassen, Selig, and Malm¹⁰ have studied the Raman as well as infrared absorption spectra of these two molecules and reassigned the fundamental frequencies as follows in wavenumbers: 741 (A_{1g}), 643 (E_g), 741 (F_{1u}), 264 (F_{1u}), 306 (F_{2g}), and 190 (F_{2u}) for molybdenum hexafluoride and 755 (A_{1g}), 596 (E_g), 715 (F_{1u}), 257 (F_{1u}), 246 (F_{2g}), and 193 (F_{2u}) for rhenium hexafluoride. These authors have also calculated the statistical thermodynamic functions for these two molecules. On the basis of these new fundamental frequencies, Nagarajan¹¹ has very recently studied the mean amplitudes of vibration. In the present investigation these two molecules with their latest vibrational data have been taken for the evaluation of potential constants.

Gold, Dowling, and Meister¹² treated the problem of the redundant symmetry coordinates in the analyses of molecular vibrations and explained that one can make use of the redundant symmetry coordinates to obtain a unique set of force constants consistent with the symmetry force constants. If one assumes the most general quadratic potential energy function, the analytical expressions relating the valence force constants(f) to the symmetry force constants(F) may be obtained from the transformation, $f = U'FU$, where U is the matrix formed in the symmetry coordinates, U' is the transpose of U matrix and f and F are also the force constant

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² Gaunt, J. *Trans. Faraday Soc.*, 1954, **50**, 209.

³ Burke, T. J., Smith, D. F., and Nielsen, A. H., *J. Chem. Phys.*, 1952, **20**, 447.

⁴ Venkateswarlu, K., and Sundaram, S., *Z. phys. Chem. N. F.* 1956, **9**, 174.

⁵ Pistorius, C. W. F. T., *J. Chem. Phys.*, 1958, **29**, 1328.

⁶ Nagarajan, G., *Bull. Soc. Chim. Belg.*, 1962, **71**, 77.

⁷ Nagarajan, G., *Bull. Soc. Chim. Belg.*, 1962, **71**, 674.

⁸ Nagarajan, G., *Bull. Soc. Chim. Belg.*, 1962, **71**, 716.

⁹ Sundaram, S., *Z. phys. Chem. N. F.*, 1962, **32**, 219.

¹⁰ Claassen, H. H., Selig, H., and Malm, J. G., *J. Chem. Phys.* 1962, **36**, 2888, 2890.

¹¹ Nagarajan, G., *Curr. Sci.*, 1963, **32**, 64.

¹² Gold, R., Dowling, J. M., and Meister, A. G., *J. Mol. Spectroscopy*, 1958, **2**, 9.

matrices. This principle has been well applied by Sundaram^{13,14} for the ammonium and borohydride ions and by Nagarajan¹⁵ for silyl halides. Recently, Nagarajan^{7,16} has approached the same problem to get the same result in a more simple manner in evaluating a unique set of valence force constants for 12 octahedral XY_6 type molecules and antimony pentafluoride and niobium pentachloride by making use of the relations $S_0^2 = 0$ and $S_0 S_i = 0$ where S_0 is the redundant symmetry coordinate and S_i an arbitrary symmetry coordinate. This principle has been applied to evaluate the potential constants of molybdenum and rhenium hexafluorides.

Following the methods outlined by Nagarajan,⁷ the secular equations giving the normal frequencies in terms of the valence force constants were constructed with the help of the potential and kinetic energy matrices according to Wilson^{17,18} and then solved. Much care was taken in solving the secular equations under the symmetry species F_{1u} . First the nondiagonal term was neglected and the two diagonal terms were easily solved. Then the values were given in succession to the nondiagonal term and systematically adjusted along with the values of the diagonal terms until they were able to reproduce the observed fundamental frequencies to the nearest wavenumbers. When the obtained force constants were introduced into the equations it was found that the calculated frequencies were in good agreement with those of the observed ones. The obtained numerical values of the valence force constants in mdyne/Å are as follows: $f_a = 4.9875$, $f_{aa} = 0.2535$, $f'_{aa} = 0.1561$, $f_\phi = 0.2900$, $f_{\phi\phi} = -f''_{\phi\phi} = 0.0810$, $f'_{\phi\phi} = -0.1045$, $f'''_{\phi\phi} = -0.2112$, $f_{a\phi} = -f'_{a\phi} = 0.4246$ for molybdenum hexafluoride, and $f_a = 4.8190$, $f_{aa} = 0.4095$, $f'_{aa} = -0.0326$, $f_\phi = 0.2181$, $f_{\phi\phi} = -f''_{\phi\phi} = 0.0551$, $f'_{\phi\phi} = -0.0815$, $f'''_{\phi\phi} = -0.2113$, and $f_{a\phi} = -f'_{a\phi} = 0.3562$ for rhenium hexafluoride, where f_a is the X-Y stretching force constant, f_{aa} the interaction force constant between two X-Y stretchings when the bonds are adjacent, f'_{aa} the interaction constant when the bonds are non-adjacent, f_ϕ the Y-X-Y bending force constant, $f_{\phi\phi}$, $f'_{\phi\phi}$, $f''_{\phi\phi}$, $f'''_{\phi\phi}$, $f_{a\phi}$, $f'_{a\phi}$, and $f''_{a\phi}$ are all the respective bending-bending and stretching-bending interaction constants. The detailed explanation of these force constants are given by Nagarajan.⁷ By symmetry of the molecular system the stretching-bending interaction constant $f'_{a\phi}$ vanish. Most of the interaction constants (stretching-stretching, bending-bending and stretching-bending) are, due to the reassigned fundamental frequencies, much deviated from those obtained by Venkateswarlu and Sundaram,⁴ Pistorius,⁵ and Nagarajan.⁷ The interaction constants $f_{\phi\phi}$ and $f''_{\phi\phi}$ in molybdenum hexafluoride and $f_{\phi\phi}$, $f'_{\phi\phi}$, $f''_{\phi\phi}$, and f'_{aa} in rhenium hexafluoride are significantly small.

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¹⁴ Sundaram, S., *Z. phys. Chem. N. F.*, 1962, **34**, 225.

¹⁵ Nagarajan, G., *Bull. Soc. Chim. Belg.*, 1962, **71**, 226.

¹⁶ Nagarajan, G., unpublished data, 1963.

¹⁷ Wilson, E. B. Jr., *J. Chem. Phys.*, 1939, **7**, 1047.

¹⁸ Wilson, E. B. Jr., *J. Chem. Phys.*, 1941, **9**, 76.