Potential Field Refinement in Some Trigonal-Bipyramidal Molecules

Sir:

The new vibrational amplitudes for some trigonal-bipyramidal molecules made available in the preceding note by Bartell[1] show ranges for F_{eq}–F_{eq} and F_{eq}–F_{ax} nonbonded distances which are intermediate for the most part between values expected for the two force fields recently discussed by us[2,3] as well as others[4] (assignment A [ν(equatorial in-plane bend) > ν(axial bend)] and assignment B [ν(axial bend) > ν(equatorial in-plane bend)].

Lack of sufficient spectroscopic data made necessary normal-coordinate calculations focused primarily on the diagonal force constants. As a consequence of the underdetermined character of the potential function two acceptable fields resulted. Actually a considerable range of force fields between these two "extremes" is possible. Certain physical arguments were cited[2,3] favoring field A while others, Coriolis coefficients, favored field B. As a result no conclusion regarding the "correct" field was given.

What the new amplitude data suggest is an importance associated with interaction force constants. For example, strong coupling of axial and equatorial bending coordinates would tend to equate the F_{ax}–F_{eq} and F_{eq}–F_{eq} amplitudes in a normal-coordinate calculation over that provided by either field A or B. In this way agreement with the diffraction amplitudes[1] may be achieved.

Thus, we calculate a best fit in the case of PF_5[5] where the low-frequency bending mode ν_7 (179 cm^{-1}) is described as made up of 55% equatorial in-plane bending and 45% axial bending motion in terms of the potential energy distribution. In a similar manner, the high-frequency bending mode ν_6 (533 cm^{-1}) of e′ symmetry exhibits strong coupling between axial bending (37%) and equatorial antisymmetrical stretching (53%) motions in addition to some contribution from the equatorial in-plane bend (10%). The e′ stretching mode (1026 cm^{-1}) couples 75% antisymmetric stretching with about 25% axial bending coordinates.

The above mode descriptions make more understandable the appearance of particularly low-bending frequency fundamentals in pentacoordinated molecules in comparison to bending frequencies for other coordination numbers involving these same central atoms and ligands.[6] In other simple coordination numbers two bending coordinates of the same symmetry are not available for such effective coupling. Instead, the more usual bend–stretch interaction of the type indicated for the 533-cm^{-1} frequency for PF_5 is possible. The presumably weaker axial bonds[7] indicated to be involved in the coupled bending vibration are expected to influence the magnitude of the associated frequency. However, other factors emphasized by Bartell[1] undoubtedly contribute as well.

As pointed out previously[3] the low-frequency fundamental to a large measure is thought to make up the intramolecular exchange coordinate for those molecules where evidence exists for such a process. It now appears that this motion is more nearly an equal mixture of equatorial and axial bending coordinates than that suggested by either field A or B.[3,4] Such a pseudo-rotational motion is just that first suggested by Berry[8] to explain the nmr spectrum of PF_5.

Further, the lack of intensity in the infrared spectrum for the low-frequency fundamental in PF_5,[9] VF_5,[10] and others[4d] is reasonably explained. Opposing dipoles are expected to arise from the opposite movements of equatorial and axial ligands and may lead to a very low net dipolar change accompanying the vibration.[11]

The importance of anharmonicity may be considerable in analyzing amplitude variations, especially in view of the presence of low-frequency fundamentals. However, data at hand do not allow this refinement of the vibrational potential function.

DEPARTMENT OF CHEMISTRY R. R. HOLMES
UNIVERSITY OF MASSACHUSETTS J. A. GOLEN
AMHERST, MASSACHUSETTS 01002

RECEIVED FEBRUARY 16, 1970

---

[1] L. S. Bartell, *Inorg. Chem.*, **9**, 1594 (1970).

[2] R. R. Holmes and R. M. Deiters, *J. Chem. Phys.*, **51**, 4043 (1969).

[3] R. R. Holmes, R. M. Deiters, and J. A. Golen, *Inorg. Chem.*, **8**, 2612 (1969).

[4] (a) L. C. Hoskins and R. C. Lord, *J. Chem. Phys.*, **46**, 2402 (1967); (b) P. C. Van Der Voorn, K. F. Purcell, and R. S. Drago, *ibid.*, **43**, 3457 (1965); (c) S. J. Cyvin and J. Brunvoll, *J. Mol. Struct.*, **3**, 151 (1969); (d) G. L. Carlson, *Spectrochim. Acta*, **19**, 1291 (1963).

[5] Previously[2] we supported assignment B over A for PF_5, the only case where electron diffraction amplitude data had been reported: K. W. Hansen and L. S. Bartell, *Inorg. Chem.*, **4**, 1775 (1965).

[6] (a) G. M. Begun and A. C. Rutenberg, *ibid.*, **6**, 2212 (1967); (b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[7] (a) R. D. Brown and J. B. Peel, *Australian J. Chem.*, **21**, 2617 (1968); (b) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, **22**, 231 (1968).

[8] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

[9] R. M. Deiters and R. R. Holmes, *ibid.*, **48**, 4796 (1968).

[10] H. H. Claassen and H. Selig, *ibid.*, **44**, 4039 (1966).

[11] Hoskins and Lord[4a] suggested this notion but applied it to an incorrect assignment for ν_7 for PF_5 according to ref 9.