Intramolecular Exchange in Vanadium Pentafluoride

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Summary Anharmonicity data derived from observed hot band structure for the ν_7 fundamental of VF_5 has resulted in a 1·8 kcal/mol (7·7 kJ mol^{-1}) barrier associated with the intramolecular ligand exchange process.

THE determination of barrier energies inhibiting intramolecular ligand exchange in symmetrical trigonal bipyramidal molecules like PF_5, VF_5, and $Fe(CO)_5$ has been hampered by lack of appropriate experimental data.[1,2] For non-transition-element MX_5 derivatives, n.m.r. equivalence of ligand positions is maintained down to the lowest temperatures studied (−197° for PF_5[3]). Only in the case of the ionic complex $[Rh(P(OMe)_3)_5]^+BPh_4^-$ have low temperature n.m.r. data been interpreted[4] in terms of 'stoppage' of ligand exchange. Vibrational data[1,5] have shown that the simple bending process first described by Berry[6] (pseudorotation) represents a low-energy pathway. However, some uncertainty[1,7] arises in scaling the potential function because of the lack of knowledge of anharmonic effects on the exchange co-ordinate.

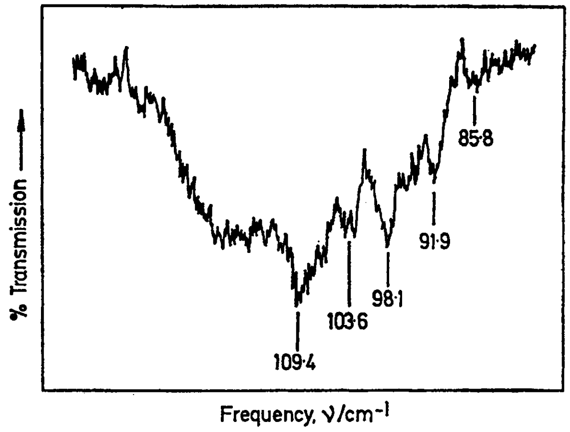

FIGURE. The ν_7 fundamental for VF_5.

TABLE 1

Upper vibrational states for the ν_7 fundamental of VF_5 (cm^{-1})

Observed	Calculated	Δ	Transition
109·4	107·9	1·5	$0 \rightarrow 1$
103·6	103·6	0·0	$1 \rightarrow 2$
98·1	98·7	−0·6	$2 \rightarrow 3$
91·9	92·9	−1·0	$3 \rightarrow 4$
85·8	85·7	0·3	$4 \rightarrow 5$
	85·2		$4 \rightarrow 5$

Reported here are spectroscopic observations which we believe allows, for the first time, a reliable determination of the potential function governing exchange. The Figure shows the ν_7 fundamental of VF_5 observed at 160 mm in a 10 cm pathlength Monel metal gas cell fitted with polyethylene windows. Previously, normal co-ordinate treatments[1,5] have indicated that the motion associated with this co-ordinate closely models the pseudorotational process and, consequently, provides an adequate description of the postulated exchange process.

The structure appearing to the low frequency side of the centre frequency represents a series of hot bands imposed on a typical PQR band. Since these bands arise from transitions of upper levels, their frequencies provide a measure of the anharmonicity of the vibrational mode. It is fortunate that the frequency is so low. As a result, several of the levels are sufficiently populated (Boltzman distribution) to allow the corresponding transitions to be observed.

A mixed quartic-harmonic function[8] $V = A(Z^4 + BZ^2)$, previously tested on SF_4,[9] describes a double-minimum potential suitable for the problem at hand. It has been applied extensively to pseudorotational processes observed in ring systems where much more complete spectral data are available.[10] Thus, greater confidence is gained in its application here over other functions that might be used to fit the data.

The exchange co-ordinate is related to Z which is a function of the distance along a C_2 axis between the central atom and the midpoint intersection of a line connecting two of the equatorial fluorine atoms. Fitting the transitions observed in the Figure with eigenvalue differences for the mixed potential function results in the expression $V = 9{\cdot}82\,(Z^4 - 16{\cdot}2\,Z^2)$ describing the exchange co-ordinate. The resultant barrier energy is $1{\cdot}84 \pm 0{\cdot}7$ kcal/mol ($7{\cdot}7 \pm 2{\cdot}9$ kJ mol^{-1}). Table 1 lists the observed and calculated frequencies.

As described, the barrier has been obtained without reference to any specific exchange model but we prefer to associate it with the Berry process because of the mode description for ν_7 obtained from a normal co-ordinate analysis[1,5c] as well as the force-field preference stemming from electron diffraction[11] amplitude values.

In view of the double minimum potential, the levels below the barrier, of which there are seven, are doubly degenerate for the one-dimensional model we have used. For a barrier this low, as seen from Table 1, a splitting of 0·5 cm^{-1} for the $4 \rightarrow 5$ transition is calculated. Although a doublet character with a separation of 0·6 cm^{-1} might be construed for the hot band assigned at 86·1 cm^{-1} to this transition in the Figure, we have not been able to reproduce this spectral feature sufficiently. A molecular beam study of VF_5 by Dyke *et al.*[12] indicates the presence of low-lying polar states. Coupled with the new data reported here, a search in the microwave region may reveal evidence for a tunnelling process.

If the anharmonicity observed here for VF_5 is used to 'correct' the harmonic potentials reported[7] previously for AsF_5 and PF_5, the newly scaled potentials yield barrier energies of 3·0 and 3·8 kcal/mol, respectively. For the nonexistent compound[7] PH_5, a similar calculation gives 1·6 kcal/mol. These values while admittedly subject to

TABLE 2

Pseudorotational barriers, kcal/mol

	This work	Hartree-Fock model study Ref. 13		Extended Hückel Ref. 14		*Ab-initio* Ref. 15		CNDO Ref. 16	Points-on-a-sphere Ref. 17
		with *d*	no *d*	with *d*	no *d*	with d	no *d*		
PF_5	3·8			1·4	0·7	4·8	8·5	3·5	4·6,5·7
PH_5	1·6	3·9	4·9	2·1	2·3				

some error, compare favourably with results of MO treatments[13–16] and an electron pair repulsion model[17] for PF_5 and PH_5 (Table 2). Furthermore, the barrier values show an order of nonrigidity $VF_5 > AsF_5 > PF_5$ in agreement with molecular beam work.[12]

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