Vibrational Frequencies and Valence Force Constants of First-row Transition-metal Di-fluorides

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Summary Observed antisymmetric stretch and bending frequencies and geometries are given for first-row transition-metal difluorides isolated in rare-gas matrices.

WE report the results of i.r. analyses, taken over the range 33—4000 cm.$^{-1}$, for first-row transition-metal difluorides isolated in rare-gas matrices (Table).

The data for members adjacent to this family of species, *i.e.* CaF_2[1] and GeF_2,[2] are also included for comparison. The basic experimental techniques as used by us have been given elsewhere[2-5] and the bond angles were determined by accurate measurement of isotope shifts for the ν_3 frequency. The larger bond angles[4,5] (*i.e. ca.* 165°) are sensitive to possible anharmonic effects and are therefore less reliable. The symmetric stretch (ν_1) frequencies have been observed only for CaF_2, TiF_2 (643 cm.$^{-1}$ in argon matrix), and GeF_2 and are presumably too weak for observation in the near-linear cases. Gas-phase values for ν_3 are estimated on the basis of the known matrix shifts for GeF_2 and SiF_2.[2]

From these data one calculates the valence force constants[6] (Table). For these calculations the ν_3–gas estimates and the ν_2–neon data were used. The ν_2–neon data are probably within 5 cm.$^{-1}$ of the gas-phase values and in the case of GeF_2 the matrix value is identical with the known gas-phase value.[2] Values of the stretch–stretch interaction force constant (k_{12}) are 0·11 and 0·22 mdyn./Å for TiF_2 and GeF_2, respectively, and from the related dissociation energy data[7] are thought to be of similar magnitude and sign for the other difluorides with the probable exception of CuF_2. It can be shown that neglect of both k_{12} and k_{13}, the stretching–bending interaction valence force constant, has only a minor effect on the bending force constant (k_δ/l^2), for example approximately 3% error in the case of TiF_2. Similarly a reasonable estimate of k_{13}, using for example the known SiF_2 analogy,[8] has only a minor effect on the ($k_1 - k_{12}$) values. Thus the trends in the tabulated stretching and bending force constants with the transition-element atomic number are considered meaningful.

The trend in the stretching force constant correlates remarkably well with the known trend for the energy of dissociation of MF_2 into M^{2+} and $2F^-$. The bending force constants may be expected to relate at least qualitatively with the ionic character of the M–F bonds in these species.

These data should prove useful in refining relations

Vibrational frequencies (cm.$^{-1}$) and force constants (mdyn./Å) for transition-metal difluorides[a]

	Antisymmetric stretch (ν_3)			Bending frequency (ν_2)		Valence force consts.		Bond angle
	Argon	Neon	Gas(est.)[b]	Argon	Neon	k_δ/l^2	$k_1 - k_{12}$	(degrees)
CaF_2[c]	561	581	595	(165)	—	0·089	2·17	140 ± 5
ScF_2	685·0	699·7	710	—	—	(0·102)[d]	3·34	(135)[i]
TiF_2[e]	740·1	752·8	762	171·2	176·2	0·110	4·03	130 ± 4
VF_2	733·2	742·8	750	—	158·0	0·080	3·80	(150)[i]
CrF_2	654·5	679·6	697	155·4	151·1	0·074	3·18	180 ± 8
MnF_2	700·1	722·1	740	124·8	132·0	0·058	3·67	(180)[i]
FeF_2	731·3	752·8	768	141·0	148·5	0·073	4·00	180 ± 8
CoF_2	723·5	745·8	762	151·0	157·6	0·088	4·02	(170)[i]
NiF_2[f]	779·6	800·4	815	139·7	143·0	0·069	4·57	165 ± 8
CuF_2[f]	743·9	766·5	782	183·0	187·7	0·123	4·33	165 ± 8
ZnF_2[f]	763·5	781·5	794	(150·5)[g]	—	0·088	4·48	165 ± 8
GeF_2[h]	648	655	660	262	—	0·319	3·82	95 ± 2

[a] Frequency measurements are accurate to better than ±0·5 cm.$^{-1}$.
[b] Values, estimated as described in text, are believed accurate to ±10 cm.$^{-1}$.
[c] Stretch frequencies given by A. Snelson, in ref. 1. ν_2 and bond angle measured in krypton matrix by V. Calder, D. E. Mann, K. S. Seshadri, M. Allevena, and D. White, *J. Chem. Phys.*, 1969, **51**, 2093. A gas phase ν_2 of 115 ± 5 cm.$^{-1}$ has been reported by V. I. Baikov, *Optics and Spectroscopy*, 1968, **25**, 194.
[d] Interpolated value from plots of force constant against atomic number.
[e] The stretch frequencies and bond angles are reported in ref. 4.
[f] The stretch frequencies and bond angles are reported in ref. 5.
[g] Measured in a krypton matrix, A. Loewenschuss, A. Ron, and O. Schnepp, *J. Chem. Phys.*, 1968, **49**, 272.
[h] The stretch frequencies, bond angles, and a gas-phase ν_2 value of 263 ± 5 cm.$^{-1}$ are reported in ref. 2.
[i] Estimated.
[j] In some cases the ν_2 frequencies showed a matrix splitting effect of less than 8 cm.$^{-1}$ and the values listed here are for the highest requencies.

between force constants and other molecular parameters. Also, the frequency and geometry data allow the calculation of more accurate entropies for these species. The most important remaining question to be answered for many of these transition-metal difluorides is the exact nature of the ground and low-lying electronic states.

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