

MATRIX ISOLATION INFRARED SPECTROSCOPY
OF HIGH TEMPERATURE SPECIES

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Matrix isolation in rare gases has been widely used for infrared studies of reactive species. An advantage of matrix isolation for infrared studies of high temperature species is apparent if one compares the usual band widths of gas phase absorption spectra to those obtained in matrix isolation spectra. In fact the narrow band widths often make possible accurate isotope shift measurements of vibrational bands which in turn can be used to calculate accurate force constants. For XY_2 triatomic molecules isotope shifts of the antisymmetric stretch (ν_3) can often set close limits on the bond angle. Alternatively, isotope shifts of the ν_1 and ν_2 can be used in combination to determine the bond angle but the measurements are sometimes made difficult because of their relatively low absorption intensities.

A simple use may be made of the isotope shifts of some diatomic molecules to determine their anharmonicity. A comparison of the measured anharmonicity of a molecule trapped in a rare gas matrix to its gas phase value serves as an indication of the effect of the matrix on the shape of the potential energy curve. The following table lists $\omega_e x_e$ for matrix isolated, using Ne or Ar, and gas phase molecules.

| | $\omega_e x_e$ (cm^{-1}) | |
|------|-------------------------------------|-----------|
| | matrix isolated | gas phase |
| LiF | 9.4 ± 1 | 8.0 |
| LiCl | 3.1 ± 1 | 4.2 |
| SiO | 7.8 ± 3 | 6.0 |

It is clear from the above table that anharmonicities are affected only a very small amount, if at all, by a rare gas matrix. This is true for LiF even though the ν_e value shifts about 50 cm^{-1} from the gas phase to an argon matrix.

Isotope shift measurements of the ν_3 for symmetric triatomic XY_2 molecules may be exactly related to the bond angle by the following equation:

$$\sin \alpha = \frac{\left[\frac{M_x (M_y w_3^2 - M_y^i w_3^{i2})}{2M_y M_y^i (w_3^{i2} - w_3^2)} \right]^{1/2}}$$

where 2α equals the bond angle and w_3 is the zero-order antisymmetric stretch frequency. In practice one uses measured ν_3 values and estimates the anharmonic effect which in most cases has little influence on the measured bond angle.

It also follows from the above equation that a $\pm 0.1 \text{ cm}^{-1}$ error in the isotope shift measurement of ν_3 will cause a bond angle close to 180° to be less well determined than one close to 90° . The effect is such that with present instruments it becomes difficult to distinguish between bond angles of 160° and 180° . Although for these cases an isotope shift measurement can clearly establish a lower limit. The triatomic molecules listed in the following table have been studied in our laboratory and for the few cases (eg. NiF_2 , CuF_2 and ZnF_2) where these molecules have also been studied by other investigators the agreement with our work is very good.

| | Bond Angles (degrees) | | |
|----------------|-----------------------|------------------|--------------------------|
| | <u>This work</u> | <u>Microwave</u> | <u>This work</u> |
| SO_2 | 117 ± 2 | 119.3 | ZnF_2 160 - 170 |
| SeO_2 | 110 ± 3 | 113.5 | CuF_2 163 - 170 |
| TeO_2 | 110 ± 2 | - | NiF_2 154 - 167 |
| SiF_2 | 100.5 ± 2 | 100.9 | FeF_2 155 - 170 |
| GeF_2 | 94 ± 2 | - | CrF_2 160 - 180 |

| | Bond Angles (degrees) | | |
|------------------|-----------------------|------------------|-----------------------|
| | <u>This work</u> | <u>Microwave</u> | <u>This work</u> |
| SnF ₂ | 92 [±] 3 | - | MnCl ₂ 180 |
| TiF ₂ | 120 [±] 4 | - | VCl ₂ 180 |

It is apparent from the above data that the bond angle decreases slightly as the central atom size is increased down a column of the periodic table. One also notes that all of the isoelectronic 18 valence-electron molecules listed above are bent as predicted by Walsh rules. The bent configuration of TiF₂ indicates that its d-electrons are involved in the bonding to a considerable extent.

Infrared absorption data obtained for Group IV difluorides, SiF₂, GeF₂, SnF₂, and PbF₂ are given in the following table along with other molecular parameters. The force constants for GeF₂, SnF₂ and PbF₂ were calculated with the assumption of a zero stretch-bend interaction. The force constant values for CF₂ are taken from Milligan and Jacox J.C.P. 48, 2265, (1968) and for SiF₂ from V. M. Khanna et al J.C.P. 47, 5031 (1967).

| mdyn/Å | CF ₂ | SiF ₂ | GeF ₂ | SnF ₂ | PbF ₂ |
|---|-----------------|------------------|-------------------|-------------------|------------------|
| k ₁ | 6.0 | 5.02 | 4.07 | 3.52 | 3.02 |
| k ₁ /l ² | 1.40 | 0.44 | 0.32 | 0.16 | 0.11 |
| k ₁₂ | 1.45 | 0.31 | 0.22 | 0.17 | 0.10 |
| r _{X-MX} (Å) | 1.30 | 1.595 | (1.73) | (1.92) | (2.01) |
| bond angle | 104.9 | 100.9 | 94 [±] 4 | 92 [±] 3 | (90) |
| D _{X-MX} (kcal/mole) | 108 | 153 | 115 | 114 | 104 |
| k ₁ r _{X-MX} / D _{X-MX} (x 100) | 7.2 | 5.2 | 6.1 | 5.9 | 5.8 |

It is apparent from the above table that k₁ varies rather smoothly through the Group IV series this is not the case however for the D_{X-MX} energies. The ratio of k₁r_{X-MX} / D_{X-MX} might be expected to remain constant through the Group IV

series and in fact does for Ge, Sn, and Pb difluorides. The deviation of the ratio from an average value of 6 for SiF₂ and CF₂ seems to indicate a strengthening of the F-SiF bond by approximately 20 kcal and a weakening of the F-CF bond by approximately 20 kcal. A strengthening of the F-SiF bond might be attributed to some type of d-orbital involvement in the bonding. The weakening of the F-CF bond might well be due to strong fluorine-fluorine or fluorine-lone pair repulsion. It has been pointed out by others that the quite high value of the bond-bond interaction force constant for CF₂ is good evidence for strong fluorine-fluorine interaction.

Infrared data obtained for the first row transition metal dihalides are given in the following table. The gas phase frequencies have been estimated by arbitrarily adding $0.7\Delta(\text{Ne-Ar})$ to the measured frequency in a Neon-matrix. The force constants have been calculated using a three constant valence force field.

| | Transition Metal Difluorides | | $\Delta(\text{Ne-Ar})$ cm ⁻¹ | $\nu_3(\text{Ne})+0.7(\Delta)$ cm ⁻¹ | k_1-k_{12} md/A |
|------------------|---|------------------|--|--|----------------------|
| | $\nu_3(\text{Most Abundant})$ Isotope cm ⁻¹ | Neon | | | |
| Ca ⁴⁰ | 581 ^a | 561 ^a | 20 | 595 | 2.17 |
| Sc ⁴⁵ | 700.2 | 685.5 | 14.7 | 710.6 | 3.34 |
| Ti ⁴⁸ | 753.3 | 740.6 | 12.6 | 762.1 | 4.03 |
| V ⁵¹ | 743.3 | 733.7 | 9.6 | 750.0 | 3.80 |
| Cr ⁵² | 680.5 | 654.8 | 25.7 | 698.5 | 3.18 |
| Mn ⁵⁵ | 722.6 | 700.6 | 22.0 | 740.0 | 3.67 |
| Fe ⁵⁶ | 753.3 | 731.8 | 21.5 | 768.3 | 4.00 |
| Co ⁵⁹ | 746.3 | 723.6 | 22.7 | 762.2 | 4.02 |
| Ni ⁵⁸ | 801.2 | 780.6 | 20.6 | 815.6 | 4.57 |
| Cu ⁶³ | 767.0 | 744.4 | 22.6 | 782.8 | 4.33 |
| Zn ⁶⁴ | 782.0 | 764.0 | 18.0 | 794.6 | 4.48 |
| Ge | 655 ^b | 648 ^b | 7 | 660 | 3.82 |

a. A. Snelson, J. Phys. Chem., 70, 3208 (1966).

b. J. W. Hastie, R. H. Hauge, and J. L. Margrave, J. Phys. Chem. (in press) (1968).

The stretch force constants for the difluorides, dichlorides and their ratio are listed in the following table. The dichlorides of Mn, Fe, Co, Ni, Cu and Zn have been taken from Leroi et al J.C.P. 36, 2879 (1962).

| | MF_2 $k_1(\text{mdyn./\AA})$ | MCl_2 $k_1(\text{mdyn./\AA})$ | $\frac{k_1(\text{MF}_2)}{k_1(\text{MCl}_2)}$ |
|----|--|---|--|
| Ca | 2.17 | - | - |
| Sc | 3.34 | (1.88) | - |
| Ti | 4.03 | (2.27) | - |
| V | 3.80 | 2.19 | 1.74 |
| Cr | 3.18 | (1.79) | - |
| Mn | 3.67 | 1.99 | 1.84 |
| Fe | 4.00 | 2.23 | 1.79 |
| Co | 4.02 | 2.30 | 1.75 |
| Ni | 4.57 | 2.51 | 1.82 |
| Cu | 4.33 | 2.43 | 1.78 |
| Zn | 4.48 | 2.67 | 1.68 |
| Ge | 3.82 | 2.17 | 1.76 |

The ratio of stretch force constants is almost invariant and provides a convenient means of estimating the unmeasured dichloride force constants. The estimated values are bracketed in the above table.

Infrared spectra obtained for SeO_2 , TeO_2 and TeO are listed in the following table.

| | $\frac{\nu_3-1}{\text{cm}}$ | $\frac{\nu_1-1}{\text{cm}}$ | $\frac{k_1-k_1^2}{\text{mdyn./\AA}}$ |
|----------------|-----------------------------|-----------------------------|--------------------------------------|
| SeO_2 | 974 | 924 | 7.00 |
| TeO_2 | 845 | 827 | 5.75 |
| TeO | 791 | | 5.25 |

Polymeric forms of these species have also been identified in the matrices.

Mass spectrometric studies have indicated that the polymeric species **also**

exist in the high temperature vapors. However for the SiO system where the vapor species is almost completely monomeric SiO, matrix isolation leads to extensive polymerization even at relative SiO to rare gas concentrations of 1/1000. Similarly the electronically similar high temperature species, BF is difficult to isolate in these matrices.

Reactions of NaF and SiF₂ and Na + SiF₂ have been studied by co-condensation of both species. New absorption bands were observed and are tentatively assigned to NaSiF₃ and NaSiF₂. These products decomposed when the condensate was warmed to room temperature to form elemental Si and Na₂SiF₆.