

SiF₂의 적외선 흡수세기 예측

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Prediction of Absolute Infrared Intensities for the Fundamental Vibration of SiF₂

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요 약. 여러 플루오르화물의 플루오르 원자극성텐서를 이용하여 SiF₂의 기본 진동수에 대한 적외선 흡수세기를 예측하였는데, 예측된 상대 세기치는 보고된 스펙트럼과 잘 일치하였다.

ABSTRACT. Absolute infrared intensities are predicted for the vibrational bands of gas-phase SiF₂ using a fluorine atomic polar tensor transferred from various fluorine compounds. The predicted relative intensities agree well with published spectra of gas-phase SiF₂.

INTRODUCTION

Recently, interest in the spectroscopy of SiF₄ has been stimulated by the fact that its ν_3 fundamental at 1031cm⁻¹ overlaps the P branch of the 9.4 μ m band of the CO₂ laser.^{1,2} Pumping SiF₄ with laser radiation has led to numerous studies of, especially, dissociation³⁻⁷ and silicon isotope separation⁸, in which SiF₂ is believed to be an important chemical species, but accurate laboratory measurements of line intensities are difficult to determine because of the high reactivity of SiF₂. For this reason it is of interest to estimate theoretically the absolute band intensities of the vibrational modes of SiF₂. From these predicted band intensities, the individual line intensities in the vibrational-rotational manifolds can then in principle be calculated⁹.

Absolute band intensities may be predicted in

two ways. One method is to calculate quantum mechanically the band strength. Another approach is to derive intensity parameters for atoms or bonds in small molecules for which the experimental intensities are known, and then to transfer these parameters to similar structural units in the molecule of interest. Intensity parameters which have been transferred successfully include both electro-optical parameters^{10,11} and atomic polar tensors.^{12,13} The intensity parameters used here are the atomic polar tensors (APT's). The APT derived for fluorine has already been applied to predict infrared intensities for such molecules as SF₆ and UF₆¹⁴, and the XF₅ series¹⁵ resulting in the predicted intensities within a factor of 2 of the experimental values. Here, the absolute intensities predicted for SiF₂ using the fluorine APT's from various fluorine compounds will be presented.

METHOD OF CALCULATION

In the rigid rotor-harmonic oscillator approximation¹⁶, the absolute band intensity of the *i*-th normal mode is proportional to square of the vector dipole moment derivative with respect to the *i*-th normal coordinate, $\partial P/\partial Q_i$. Thus, to predict absolute intensities for a molecule, one must calculate the dipole moment derivatives. The relationship of the dipole moment derivatives with respect to the normal coordinates to the dipole moment derivatives in Cartesian coordinate space is expressed as follows,¹³

$$P_Q = P_X A L, \quad (1)$$

where P_Q is the matrix of the components along the molecule-fixed principal axes of the dipole

moment derivatives with respect to the 3N-6 normal coordinates. The P_X matrix in Eq. (1) is formed by the juxtaposition of the *N* atomic polar tensors of the molecule, and *A* is the symmetrized *A* matrix which transforms a set of molecule-fixed symmetry displacement coordinates to a set of space-fixed Cartesian coordinates.

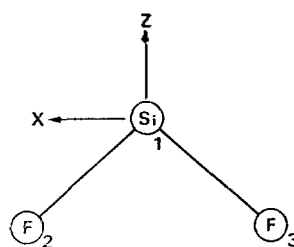


Fig. 1. Molecular Cartesian coordinate system. A right-handed coordinate system has been employed throughout the calculations.

Table 1. Atomic polar tensors for SiF₂ expressed in the principal axis system [Fig. 1].^a Units are electrons(*e*)

Fluorine APT transferred from	$P_X(F_2)^b$	$P_X(Si)^c$
SiF ₄ ^d	$\begin{bmatrix} -0.643 & 0 & 0.181 \\ 0 & -0.425 & 0 \\ 0.181 & 0 & -0.575 \end{bmatrix}$	$\begin{bmatrix} 1.286 & 0 & 0 \\ 0 & 0.850 & 0 \\ 0 & 0 & 1.150 \end{bmatrix}$
CH ₃ F ^e	$\begin{bmatrix} -0.66 & 0 & 0.33 \\ 0 & -0.26 & 0 \\ 0.33 & 0 & -0.53 \end{bmatrix}$	$\begin{bmatrix} 1.32 & 0 & 0 \\ 0 & 0.52 & 0 \\ 0 & 0 & 1.06 \end{bmatrix}$
CF ₄ ^f	$\begin{bmatrix} -0.68 & 0 & 0.29 \\ 0 & -0.33 & 0 \\ 0.29 & 0 & -0.57 \end{bmatrix}$	$\begin{bmatrix} 1.36 & 0 & 0 \\ 0 & 0.66 & 0 \\ 0 & 0 & 1.14 \end{bmatrix}$
SF ₆ ^g	$\begin{bmatrix} -0.731 & 0 & 0.308 \\ 0 & -0.358 & 0 \\ 0.308 & 0 & -0.613 \end{bmatrix}$	$\begin{bmatrix} 1.462 & 0 & 0 \\ 0 & 0.716 & 0 \\ 0 & 0 & 1.226 \end{bmatrix}$
CNDO ^h	$\begin{bmatrix} -0.818 & 0 & 0.697 \\ 0 & 0.024 & 0 \\ 0.475 & 0 & -0.687 \end{bmatrix}$	$\begin{bmatrix} 1.636 & 0 & 0 \\ 0 & -0.048 & 0 \\ 0 & 0 & 1.374 \end{bmatrix}$

^a The atomic polar tensor is defined as¹³

$$P_X(\alpha) \equiv \begin{bmatrix} \partial P_X/\partial X_\alpha & \partial P_X/\partial Y_\alpha & \partial P_X/\partial Z_\alpha \\ \partial P_Y/\partial X_\alpha & \partial P_Y/\partial Y_\alpha & \partial P_Y/\partial Z_\alpha \\ \partial P_Z/\partial X_\alpha & \partial P_Z/\partial Y_\alpha & \partial P_Z/\partial Z_\alpha \end{bmatrix}$$

^b The APT for F₃ is obtained by reversing the signs of the off-diagonal elements in $P_X(F_2)$. ^c Silicon APT calculated from the constraints on the APT's (see text). ^d Taken from ref. (18). ^e Taken from ref. (19). ^f Taken from ref. (19). ^g Taken from ref. (20). ^h These tensors were calculated using the INCNDO program 141 from QCPE, following the procedure given in ref. (13).

Finally, L is the matrix of the eigenvectors of the GF product matrix.¹⁶ Thus, from a set of APT's and normal coordinates for a molecule, absolute intensities can be predicted for each of the normal modes of vibration.

Absolute intensities were calculated for SiF₂ under the assumption that the fluorine APT's from various fluorine compounds (SiF₄, CH₃F, CF₄, and SF₆) were transferable to the fluorine atoms of SiF₂. These four choices for the fluorine (F₂ in Fig. 1) APT in SiF₂ are given in Table 1; the APT's are expressed relative to the principal axis system¹⁷ used in the normal coordinate analysis shown in Fig. 1. The APT for F₃ may be obtained by reversing the signs of the off-diagonal elements in the APT for F₂ given in Table 1. The silicon APT in SiF₂ is obtained from a consideration of the null relationship¹³ (that is, the summation of the APT's extending over all the atoms of the molecule should be a null tensor). Table 1 includes also the CNDO calculated tensors in SiF₂.

RESULTS AND DISCUSSION

The structural data used in this work are represented in Table 2. The absolute band intensities predicted for the vibrational modes of SiF₂ using APT's transferred from various fluorine compounds in Table 1 are given in Table 3. Considering first the symmetric Si-F stretching mode, one finds that transferring the fluorine APT's from various symmetric top molecules makes relatively little difference in the intensity predicted for ν_1 , so a value of around 80 km/mole appears to be a reasonable estimate. On the other hand, a larger variation is observed in the intensity predicted for ν_1 , with the theoretical CNDO calculated value predicting an intensity about twice as large as that predicted by the fluorine APT transferred from SiF₄. The intensity predicted for the antisymmetric

Table 2. Structural parameters and physical constants used in the prediction of the integrated intensities of SiF₂

Masses (u) ^a : $m_F=18.9984033$	$m_{Si}=27.976928$
Structure ^b : $R_{Si-F}=0.15901\text{nm}$	$\text{FSiF}=100^\circ 46'$
Symmetry coordinates:	
$S_1=1/\sqrt{2}(r_1+r_2)$	$r_1=\Delta r(1, 2)^c$
$S_2=\alpha$	$r_2=\Delta r(1, 3)$
$S_3=1/\sqrt{2}(r_1-r_2)$	$\alpha=\Delta\alpha(2, 1, 3)$
Normal coordinates ($u^{-1/2}$):	
L	Q_1^d Q_2 Q_3
S_1	0.285761 0.006602 0
S_2	-0.115040 0.248911 0
S_3	0 0 0.308314
Symmetrized A matrix ^e :	
1 3	-0.409644 3 1 0.259682 3 2 -0.352733
4 1	0.544705 4 2 0.506963 4 3 0.301620
6 1	-0.191203 6 2 0.259716 6 3 -0.249669
7 1	-0.544705 7 2 -0.506963 7 3 0.301620
9 1	-0.191203 9 2 0.259716 9 3 0.249669

^aRef(21). ^bRef(22). ^cThe atomic numbering is indicated in Fig. 1. ^dCalculated from the force field in ref(22) and ref(23). The labels Q_1 , Q_2 , and Q_3 correspond to the symmetric Si-F stretching, symmetric FSiF bending, and antisymmetric Si-F stretching modes, respectively. ^eThe A element for a bond stretch is unitless, and Å for a bending coordinate. Only the nonzero elements are listed. The order is row number, column number, matrix element.

Si-F stretching mode from the fluorine APT from various fluorine compounds ranges around 110 km/mole with uncertainty of 20 km/mole. Once again the CNDO calculated value is almost two times larger than the mean value obtained from the fluorine APT's of various molecules.

Such a variation would, however, be acceptable considering the notorious difficulty in quantitative prediction of dipole moment derivatives from approximate quantum mechanical treatments. In fact, the CNDO calculated value for the intensity of the Si-F stretching mode in SiF₄ is 50% larger than that from experiment.¹⁸ Thus, a reasonable estimate (within 50%) for

the absolute intensity of ν_1 and ν_3 in SiF₂ would appear to be about 80 km/mole and 110 km/mole, respectively. Moreover, present intensity calculations indicate that the ν_3 mode has the absolute intensity greater (~1.5 times) than that of the ν_1 mode consistent with the qualitative feature of Khanna *et al.*'s infrared spectrum of SiF₂.²⁵ This observation suggests that APT method would help reducing errors in the measurement of the integrated intensities of two strongly overlapping bands as ν_1 and ν_3 in SiF₂.

No quantitative estimates have been made for the absolute intensity of the bending mode ν_2 of SiF₂. Calculations presented here predict the FSiF bending to be the least intense feature in the infrared spectrum. The fluorine APT for SiF₂ transferred from SiF₄ predicts an absolute intensity that is almost twice as large as the value predicted either by the fluorine APT's of other fluorine compounds or by the CNDO calculation. A reasonable estimate (within 50%) for the absolute intensity of ν_2 would, however, appear to be about 10 km/mole.

The sum of the absolute intensities predicted by the calculation using the fluorine APT transferred from SiF₄ is 177 km/mole, while the intensity sums predicted by the calculation using the fluorine APT's transferred from CH₃F, CF₄, and SF₆ are 191, 203, 232 km/mole, respectively. These predicted intensity sums suggest

Table 3. Absolute infrared intensities predicted for SiF₂

Mode (cm ⁻¹)		Fluorine APT from (units are km mole ⁻¹) ^a				
		SiF ₄	CH ₃ F	CF ₄	SF ₆	CNDO
ν_1 (855)	ν_1 (SiF)	68	74	79	90	131
ν_3 (870)	ν_{as} (SiF)	94	112	115	132	212
ν_2 (345)	δ_s (FSiF)	15	5.3	8.8	10	6.6

^aThe absolute intensity is defined experimentally as $(1/Cl) \int \ln(I_0/I) d\nu$.

that the actual experimental sum of the absolute band intensities for SiF₂ may be estimated as 201 ± 31 km/mole.

The YY components in the APT's of SiF₂ depend solely on the equilibrium dipole moment of SiF₂. The value of $P_{YY}(F_2)$ predicted from the equilibrium dipole moment of SiF₂²⁴ is -0.606e. As shown in Table 1, $P_{YY}(F_2)$ of SiF₂ from SiF₄ is 30% lower than the experimental one, while other sets make even larger difference in the value of $P_{YY}(F_2)$. Moreover, CNDO calculated value has opposite sign in comparison with the experimental result. These considerations suggest strongly that the absolute band intensities predicted for the vibrational modes of SiF₂ using APT's transferred from SiF₄ would be the preferred one. This may be consistent with the argument that the bonding environment of the fluorine atoms in SiF₂ would rather be similar to SiF₄ than other fluorine compounds considered here such that the fluorine APT should be transferred to SiF₂ from SiF₄.

In conclusion, the absolute intensities calculated for SiF₂ using the fluorine APT transferred from SiF₄ are probably accurate to within a factor of 2 for most of the vibrational bands. The relative intensities calculated here seem certainly consistent with published infrared spectra of gas-phase SiF₂. The present calculation exhibits, in addition, that one should be careful in using the approximate CNDO method to predict the absolute intensities for vibration of polyatomic molecules.

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