I. INTRODUCTION

Since the first observation of infrared photodissociation of a van der Waals (vdW) molecule by Scoles et al.,1 numerous vdw molecules produced in a molecular beam have been studied with the use of photodissociation action spectroscopy.2 Using sulfur hexafluoride (SF6), Reuss and co-workers monitored the predissociation-induced intensity depletion of a beam of SF6 clusters, interacting with tunable infrared laser radiation. They demonstrated that, in the dimer, the degenerate \( \nu_3 \) vibrational band of SF6 is split into a doublet, mainly because of the dynamical dipole–dipole interaction.3–6 Similar studies were extended to the (SiF4)2 and (SiH4)2 systems and the spectral data were analyzed in terms of not only the dipole–dipole but also of the dipole–induced-dipole interactions.5–8 Meanwhile, Urban and Takami observed the rotationally resolved spectra of (SF6)2 to conclude that the structure of the dimer is of D\(_{2h}\) symmetry.9 Scoles et al. further developed a novel technique to study liquid helium droplets10 and molecular hydrogen clusters11 that incorporated SF6 as a probe. The observed spectra were attributed to the monomer and the dimer of SF6.10,11 Subsequently, the rotational structure of the spectral feature reported by Scoles et al. was resolved by Toennies and co-workers by employing a continuously tunable laser.12–16

Guided by this work we have attempted to observe the vibrational absorption spectrum of SF6 clusters in solid parahydrogen (\( p-H_2 \)) at cryogenic temperatures. Solid parahydrogen is useful in matrix isolation spectroscopy because the intermolecular interaction between guest molecules and surrounding hydrogen molecules is very weak. This characteristic is demonstrated by our observation of the highly resolved rotation–vibration spectra of CH4 and CD4 in the \( p-H_2 \) matrix.17–19 In the CH4/\( p-H_2 \) system we found that the matrix-isolated CH4 monomer exhibits fine spectral splittings which provide us with quantitative information on the subtle intermolecular interaction between the CH4 molecule and the matrix.20 Not only the isolated monomer but also clusters of CH4 show a rather rich spectral structure21 that indicates that the parahydrogen matrix is also useful for the study of molecular clusters.

Recently, Fajardo et al. observed the spectra of (H2O)\( n \)/\( p-H_2 \) for sizes up to the hexamer.22 They reported the existence of a cyclic hexamer in the solid parahydrogen matrix in addition to the cage hexamer which is produced in a supersonic expansion. The cyclic hexamer of water had been reported in liquid helium droplets23 but has never been found in the gas phase. The result of Fajardo et al. indicates the presence of a similarity between solid parahydrogen matrices and liquid helium droplets.

In the present work, our primary aim is to obtain the direct absorption spectrum of SF6 and its clusters in solid \( p-H_2 \), rather than the photodissociation action spectrum in the molecular beam as in the previous studies. We expected rotationally resolved spectra for SF6 monomers in solid \( p-H_2 \), as in the case of the CH4/\( p-H_2 \) system. However, it turned out that such a molecular rotation was not found in the SF6/\( p-H_2 \) system. This is reasonable because the rotational constant of SF6, \( B_{SF6} = 0.09 \text{ cm}^{-1} \), is about one-fiftieth of the rotational constant of methane, \( B_{CH_4} = 4.8 \text{ cm}^{-1} \). The large rotational constant of CH4 allows the methane molecule to rotate almost freely to exceed the anisotropic potential barrier on account of the surrounding hydrogen molecules, while the small rotational constant of SF6 may prevent the molecule from free rotation to exceed the similar or probably even higher potential barrier than that for CH4. Despite this failure to obtain the rotationally resolved spectrum of SF6, we have succeeded in procuring significant spectral information on SF6 clusters of several sizes.

II. EXPERIMENTAL PARTS

A. Preparation of the sample and measurements

Solid SF6/\( p-H_2 \) samples were prepared using two methods. One is the closed-cell method which was adopted in our previous work.17,18 A brief recapitulation of this is as follows: A variable concentration gaseous mixture of SF6 and \( p-H_2 \) was slowly introduced through a 1/16-inch stainless tube into a copper cell having a cavity of a diameter of 2.0 cm and an optical path length of 3.0 cm over a period of...
approximately 2.5 hours. Both ends of the cavity were sealed with BaF$_2$ windows with indium gaskets. The cell was attached to the flat base of a liquid helium cryostat with a temperature-controllable spacer. The temperature of the cell was set at 8.5 K to ensure optimum epitaxial growth of an optically transparent mixed crystal of SF$_6$/p-H$_2$. The growth of the crystal started from the surface of the cylindrical cavity toward the center of the copper cell. After the crystal was grown, the temperature was lowered from 8.5 K to 4.5 K, slowly enough to avoid cracking. From our previous work, it has been shown that the $c$ axis of the crystal is approximately parallel to the radial direction of the round cylindrical copper cell.

Another method of preparation of the solid SF$_6$/p-H$_2$ samples is the rapid-deposition method, developed by Fajardo et al., to grow transparent matrices of hydrogen. Although this rapid deposition does not guarantee the formation of neat epitaxial crystals (unlike the closed-cell method), we tried it because this method was deemed to be desirable for comparing the degree of isolation of the SF$_6$ molecules in the solid between slow and quick solidification. In the rapid deposition, an optical BaF$_2$ window was cooled to 2.9 K, which was the lowest attainable temperature in the present work. The gaseous mixture of SF$_6$/p-H$_2$ was sprayed onto the surface of the window to obtain $\sim$1 mm thick solid SF$_6$/p-H$_2$ samples in less than 20 min.

The optical measurement was carried out using a Bruker IFS-120HR Fourier-transform spectrometer with a spectral resolution of 0.25–0.01 cm$^{-1}$. An MCT (mercury–cadmium–telluride) detector was employed throughout the experiment.

### B. Experimental results

Figures 1 and 2 show the representative spectra observed for the rapid deposition and the closed-cell deposition, respectively. In both figures, the top and the bottom spectra correspond to a lower and a higher ratio of concentration of SF$_6$ to p-H$_2$, respectively.

The molar ratios of SF$_6$/p-H$_2$ in the premixed gaseous samples in Fig. 1 were about $1 \times 10^{-6}$ (top) and $1 \times 10^{-4}$ (bottom) as estimated by the measurement of the pressure gauge. Similarly the ratios in Fig. 2 were $1 \times 10^{-6}$ (top) and $1 \times 10^{-5}$ (bottom). The above concentrations correspond to an upper limit of the concentrations in the solidified samples because part of the SF$_6$ molecules must be lost on the chill of the wall of the stainless tube during the introduction of the premixed gas into the cell or onto the BaF$_2$ window. In this present work, however, it is not necessary to know the exact concentrations in the solid samples, but we only need to compare the relatively dilute and concentrated samples prepared by both methods of solidification. We repeated these comparative spectral measurements to obtain similar spectral patterns as those shown representatively in Figs. 1 and 2.

### III. SPECTRAL ASSIGNMENT

The monomeric SF$_6$ molecule in the gas phase shows the $\nu_3$ asymmetric stretching vibrational absorption at around 948.0 cm$^{-1}$. The absorption of the degenerate vibration splits into a doublet at about 934.0 and 956.1 cm$^{-1}$ in the gaseous dimer. Meanwhile, the monomeric SF$_6$ in liquid helium droplets exhibits the rotationally resolved $\nu_3$ band at about 946.5 $\pm$ 0.1 cm$^{-1}$. The shift of 948.0 cm$^{-1}$ to 946.5 cm$^{-1}$ between the gaseous SF$_6$ and SF$_6$ in helium droplets is quite small, which indicates that the perturbation due to the helium droplets is very weak. Monomers and dimers of SF$_6$ have also been studied in molecular hydrogen clusters.\(^{11}\) In such clusters, the monomer absorption is located at 942.0 cm$^{-1}$, which is redshifted by 6.0 cm$^{-1}$ relative to the gas phase value. The dimer shows a doublet at 928.5 and 949.6 cm$^{-1}$, comparable to the doublet at 934.0 and 956.1 cm$^{-1}$ in the gas phase, but is redshifted by about 6 cm$^{-1}$, which is similar to the monomer shift.

On the basis of this reference data, we assign the major absorption of A at 942.0 cm$^{-1}$ in the upper panel of Fig. 1 to monomeric $^{32}$SF$_6$ in solid p-H$_2$. We ignore for the moment the congested peaks flanking the absorption A. The minor absorption B is assigned to monomeric $^{34}$SF$_6$ as the intensity ratio is compatible with the ratio of the natural abundance of $^{32}$S: $^{34}$S $\approx$ 95.0:4.2. Since the concentration ratio of SF$_6$ in the sample for the lower panel of Fig. 1 is higher than that in the upper panel by a factor of $10^4$, the signal of the monomeric $^{32}$SF$_6$ (A) is out of scale, and that of $^{34}$SF$_6$ (B) is enhanced accordingly. The appearance of the new absorptions C, D, E,
and $F$ in the concentrated sample must be attributed to clusters of $\text{SF}_6$. Before considering these new absorptions we must first compare the general spectral patterns in Figs. 1 and 2, the latter being obtained for the samples prepared by the closed-cell method at 8.5 K and then kept at 4.5 K.

In Fig. 2, the absorptions $A$ and $B$ seen in Fig. 1 and assigned to the monomeric $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ are much reduced. The second point to note in Fig. 2 is that the absorptions $C$, $E$, and $F$ seen in the concentrated sample of Fig. 1 are greatly enhanced in both spectra of Fig. 2. Looking at the fine structure of the absorption $C$ in Fig. 2, we notice that in the concentrated sample there appears a strong, new absorption, labeled by $C'$, which behaves independently from $C$. The third difference between Figs. 1 and 2 is the appearance of intense absorption $G$ and weak absorptions $H$ and $J$ in both spectra of Fig. 2. Further, the difference is in the substructures of the above-mentioned major absorptions.

The separations between $C$ at 928.2–929.5 cm$^{-1}$ and $E$ at 947.5–950.5 cm$^{-1}$ in both spectra of Fig. 2 are comparable to the doublet of $C$ and $E$ in Fig. 1. They are also comparable to the doublet of gaseous ($^{32}\text{SF}_6)_2$ at about 934.0 and 956.1 cm$^{-1}$ if we assume a common redshift by about 6 cm$^{-1}$ between the gas and the solid media. The shift of 6 cm$^{-1}$ is comparable to the difference between 942.0 cm$^{-1}$ assigned to the monomeric $^{32}\text{SF}_6$ in $p$-$\text{H}_2$ solid and 948.0 cm$^{-1}$ of the $^{32}\text{SF}_6$ molecule in the gas phase. Therefore, it is reasonable to conjecture that the absorptions $C$ and $E$ in Fig. 2 and in the lower spectrum of Fig. 1 are attributed to dimeric $^{32}\text{SF}_6$ in solid $p$-$\text{H}_2$. This is also supported by the results of the study of $^{32}\text{SF}_6$-doped $\text{H}_2$ clusters, in which the dimer peaks are observed at 928.5 cm$^{-1}$ and 949.6 cm$^{-1}$. The absorption $C'$ is argued in the Discussion section.

As has been shown, the closed-cell method tends to form more clusters than the rapid-deposition method. The higher temperature of 8.5 K in the closed-cell method than the temperature of 2.9 K in the rapid-deposition method during crystal growth may favor the cluster formation in the cell method. It was consistently observed that the absorption $A$ assigned to the monomer in Fig. 2 decreased gradually when the closed-cell sample was kept at temperatures above 8.0 K. The above qualitative argument will be substantiated by an analysis of the intermolecular interaction among $\text{SF}_6$ molecules in the next section.

### IV. ANALYSIS OF OBSERVED SPECTRA

#### A. General framework of analysis

The dominant mechanism for the splitting of the $\nu_3$ band upon dimerization has been associated with the resonant dipole–dipole (DD) interaction. The contribution of the additional dipole–induced-dipole (DID) interaction was also examined not only for ($\text{SF}_6)_2$ but also for the related systems of ($\text{SiF}_4)_2$ and ($\text{SiH}_4)_2$. In the case of ($\text{SF}_6)_2$, it was concluded that the DD mechanism is dominant with only about a 10% contribution of the DID mechanism and that the contribution of the dispersion and the exchange interactions is negligible.

In agreement with the preceding work, we also assume that only the DD and DID interactions are significant in the analysis of the observed spectra. Following the previous work, we describe the triply degenerate $\nu_3$ vibrational states of ($\text{SF}_6)_n$ ($n = 2, 3, \ldots$) in terms of $3 \times n$ harmonic oscillator functions $|x_1>, |y_1>, |z_1>$, and $|x_2>, |y_2>, |z_2>$ where the symbols such as $|x_1>$ stand for the vibrational excited state in which the $x$ component of the triply degenerate mode of the $i$th molecule is excited to the $v = 1$ state. We consider the two Hamiltonians, shown in Eqs. (1) and (2) to describe the intermolecular interaction,

\[
H_{\text{DD}} = \frac{1}{4\pi \varepsilon_0} \sum_{i>j} 3(\mu_i \cdot \mathbf{R}_{ij})(\mu_j \cdot \mathbf{R}_{ij}) - \mu_i \cdot \mu_j, \tag{1}
\]

\[
H_{\text{DID}} = \frac{1}{2} \frac{1}{(4\pi \varepsilon_0)^2} \sum_{i,j} \alpha_i \mu_i \cdot \mu_j + 3(\mu_i \cdot \mathbf{R}_{ij})^2 \tag{2}
\]

Here, the symbols $\mu_i$ and $\alpha_i$ stand for the dipole operator and the isotropic polarizability of molecule $i$, respectively. The symbols $\mathbf{R}_{ij}$ and $\mathbf{R}_{ij}$ represent the distance and the unit vector connecting the sulfur atoms in molecules $i$ and $j$, respectively. Obviously, the diagonal elements of $H_{\text{DD}}$ for the ground and for the $v = 1$ vibrationally excited states vanish.
whereas the elements between the ground and the excited states give the nonzero transition dipole moment. As to the off-diagonal elements, only the terms of the kind, $\mu_i u^{H_{DD}} u_j$, $\mu_i u^{H_{DD}} u_j$, and $\mu_i u^{H_{DD}} u_j$ survive. On the other hand, the diagonal elements of $H_{DD}$ remains as non-zero for both the ground and the vibrational excited states of the dimer and larger clusters.

The transition intensity is calculated from the dipole operator, which is given as the sum of the dipole operator of the $j$th molecule plus the induced dipole at molecule $k$ as in Eqs. (3) and (4).

$$\mu_j = \mu_j^0 + \sum_k \mu_{k,j}^{\text{ind}},$$

$$\mu_{k,j}^{\text{ind}} = \frac{\alpha}{4 \pi \varepsilon_0} - \mu_k + 3(\mu_k \cdot \hat{R}_{kj})\hat{R}_{kj}.$$  

To a first order approximation, the dipole operator appearing in Eq. (4) may be replaced with the operator $\mu_k^0$, which is unaffected by molecules other than the $k$th.

B. Monomers

As is stated in Sec. III, the absorptions $A$ and $B$ are assigned to the monomeric $^{32}\text{SF}_6$ and $^{34}\text{SF}_6$ in solid $p$-H$_2$. The absorption $D$ shown in the lower spectrum of Fig. 1 is assigned to monomeric $^{33}\text{SF}_6$ because the relative intensities $A$, $B$, and $D$ are approximately proportional to the natural abundance of $^{32}\text{S}:^{34}\text{S}:^{33}\text{S} = 95.0:4.2:0.8$. In the top panel of Fig. 3 the calculated transition frequency of monomeric $^{32}\text{SF}_6$ is shown by the stick at $942.0 \text{ cm}^{-1}$, and that of $^{34}\text{SF}_6$ is shown with asterisk at $924.8 \text{ cm}^{-1}$. Both of them are shifted by $2.6 \text{ cm}^{-1}$ from the gas phase values.

Each monomeric absorption is surrounded by congested substructures in a range of a few cm$^{-1}$ around the absorption maxima. These structures cannot be associated with the rotational levels of the monomers, contrary to our initial anticipation by analogy with our work on the CH$_4/p$-H$_2$ system. At the moment, we hypothesize that the substructures are related to multiple trapping sites, crystal field splitting, and the librational motion of the monomers in limited spatial environments. A temperature-dependent change of the substructures is given in Fig. 4 and is briefly commented upon in the Discussion section below.

C. Dimers

The $v=1$ triply degenerate $\nu_5$ vibrational states are split in the dimer by $H_{DD}$ and $H_{DID}$. The explicit $6 \times 6$ matrix is...
where \( \omega_1 \) and \( \omega_2 \) are the fundamental vibrational frequencies of molecules 1 and 2, respectively. The symbols \( \Delta_{DD} \) and \( \delta_{DD} \) are defined as

\[
\Delta_{DD} = \frac{1}{4\pi \varepsilon_0 R^3} |\mu_0|^2, \tag{5}
\]

\[
\delta_{DD} = \frac{\alpha}{2(4\pi \varepsilon_0)^2 R^6} |\mu_0|^2. \tag{6}
\]

Here, the \( \mu_{01} \) is the transition moment between the ground state and one of the vibrationally excited states. The symbol \( R \) is the distance between molecules in the dimer.

In the case of the dimer of the same isotopic species, such as \((^{32}\text{SF}_6)_2\) and \((^{34}\text{SF}_6)_2\), the fundamental frequencies \( \omega_1 \) and \( \omega_2 \) in the matrix above are the same. Thus, the corresponding eigenvalues and eigenvectors can be simply expressed below, where \( \omega_0 = \omega_1 = \omega_2 \).

\[
\begin{align*}
|1\rangle & = \frac{1}{\sqrt{2}}(|z_1\rangle + |z_2\rangle) \\
|2\rangle & = \frac{1}{\sqrt{2}}(|x_1\rangle - |x_2\rangle, |3\rangle = \frac{1}{\sqrt{2}}(|y_1\rangle - |y_2\rangle) \\
|4\rangle & = \frac{1}{\sqrt{2}}(|z_1\rangle + |z_2\rangle), |5\rangle = \frac{1}{\sqrt{2}}(|y_1\rangle + |y_2\rangle) \\
|6\rangle & = \frac{1}{\sqrt{2}}(|z_1\rangle - |z_2\rangle).
\end{align*}
\]

(7)

In this case only the transitions to the eigenstates \(|1\rangle\), \(|4\rangle\), and \(|5\rangle\) are allowed by symmetry where the states \(|4\rangle\) and \(|5\rangle\) are degenerated. The transition frequencies are given as the differences between the eigenvalues of \(|1\rangle\) and \(|4\rangle\) (or \(|5\rangle\)) and the ground state energy which is stabilized by dimerization to a value of \(|0\rangle|H_{DD}|0\rangle = -12\delta_{DD} \), where \(|0\rangle\) represents the ground state. The right-hand side of Fig. 5 illustrates the energy levels of the \( \nu_3 \) mode of the dimeric SF\(_6\). It is seen that the perpendicularly polarized transition of the lower frequency is affected by the DID contribution by the amount of \(8\delta_{DD}\), while the contribution to the parallel transition of the higher frequency is \(2\delta_{DD}\).

The intensities of the allowed transitions are given by

\[
\langle 0 | \mu | 1 \rangle^2 = \left( 1 + \frac{2\alpha}{4\pi \varepsilon_0 R^3} |\mu_0|^2 \right)^2, \tag{8}
\]

FIG. 5. Schematic energy level diagram of the \( \nu_3 \) mode of SF\(_6\) dimer.
\[ \langle 0 \mid \mu \mid 4 \rangle^2 = \frac{1}{4 \pi \epsilon_0 R^3} \mu_0^2. \]  
(9)

With the experimental polarizability of \( \alpha/4 \pi \epsilon_0 = 6.54 \, \text{Å}^3 \)
and the intersulfur distance of \( R = 4.754 \, \text{Å} \), we obtain an
intensity ratio
\[ \frac{\langle 0 \mid \mu \mid 1 \rangle^2}{\langle 0 \mid \mu \mid 4 \rangle^2 + \langle 0 \mid \mu \mid 5 \rangle^2} = \frac{(1 + 0.12)^2}{2 \times (1 - 0.06)^2} = 0.71. \]  
(10)

With this intensity ratio and with the values of \( \Delta_{DD} = 7.05 \, \text{cm}^{-1} \), \( \delta_{DD} = 0.215 \, \text{cm}^{-1} \), and \( \omega_0 = 942.0 \, \text{cm}^{-1} \), the theoretical spectra of the dimer are constructed as shown in the second panel from the top of Fig. 3.

For the species \((32 \text{SF}_6)(34 \text{SF}_6)\), the fundamental frequencies \( \omega_1 \) and \( \omega_2 \) appearing in the matrix above are different, and thus the corresponding eigenvalues and eigenvectors become more complicated than Eq. (7) due to the broken symmetry of \( \omega_1 \neq \omega_2 \). There are four eigenvalues corresponding to two nondegenerate and two doubly degenerate states. In this case, all the four transitions have nonzero transition intensities. By assuming the values of \( \omega_1 = 942.0 \, \text{cm}^{-1} \) and \( \omega_2 = 924.8 \, \text{cm}^{-1} \), we obtained four calculated sticks with asterisks in the second panel of Fig. 3. The abundance ratio of the homodimer and the heterodimer is calculated to be 1.0:0.09. The intensities of the heterodimer shown in Fig. 3 are reduced according to the natural abundance of \(^{34}\text{S}\) against \(^{32}\text{S}\).

D. Larger clusters

The matrix in Sec. IV C for the dimer is expanded to 9 \times 9 for the trimer. In addition, it becomes necessary to know the geometrical arrangements of the three \( \text{SF}_6 \) molecules. For simplicity, we assume that the shape of the trimer is an equilateral triangle with the same intersulfur distance of \( R = 4.754 \, \text{Å} \) as that for the dimer. The parameters of \( \Delta_{DD} \) and \( \delta_{DD} \) are also assumed to be the same as for the dimer. Thus, the spectrum of the trimer \((32 \text{SF}_6)_3\) is predicted to have three transitions at 926.8, 951.2, and 954.4 \, \text{cm}^{-1} \) as shown in the third panel from the top of Fig. 3. Preliminary calculations indicate that the transition frequencies and their intensities of trimer are sensitive to its geometry. In Fig. 3, another isotopic species of \((32 \text{SF}_6)_2(34 \text{SF}_6)\) is also taken into account with the proper weights related to the abundances.

Similar calculations are extended to tetrarimers \((32 \text{SF}_6)_4\) and \((32 \text{SF}_6)_3(34 \text{SF}_6)\), assuming a regular tetrahedral conformation. The same parameters of \( R, \Delta_{DD} \), and \( \delta_{DD} \) as those for the dimer and trimer are assumed. Figure 3 summarizes the theoretical spectra of clusters up to the tetramer.

V. DISCUSSION

The overall assignment of the experiments are given in Table I. The two major sticks for the dimer in the second panel of Fig. 3 are located at \( \omega_0 + \Delta_{DD} - 2 \delta_{DD} \) and \( \omega_0 - 2 \Delta_{DD} - 8 \delta_{DD} \), which correspond to the difference between the eigenvalues of Eq. (7) and the ground state energy of \( -12 \delta_{DD} \). Using the adopted parameters of \( \Delta_{DD} \) and \( \delta_{DD} \), the two sticks are located at 926.1 and 948.6 \, \text{cm}^{-1} \), which are close to the doublet of the dimer in molecular hydrogen clusters (928.5 and 949.6 \, \text{cm}^{-1}).

The doublet apparently corresponds to the two absorptions \( C \) and \( E \) shown in the lower spectrum of Fig. 1 and in both spectra of Fig. 2. The complicated structure of the absorptions \( C \) and \( E \) in Figs. 1 and 2 may be attributed to the possible coexistence of different configurations of the two \( 33 \text{SF}_6 \) molecules and to the lift of the degeneracy of the excited state in the dimer.

Hence, a drastic decrease of its intensity in extremely concentrated samples.

In Fig. 2, the intensity of the monomer is drastically reduced and the dimer absorption becomes dominant to evenly reveal the heterodimer of \((34 \text{SF}_6)(32 \text{SF}_6)\), which is associated with the absorption \( F \) (cf. the leftmost stick with asterisk in the second panel of Fig. 3). In Fig. 2, the relative intensities of the absorptions \( C \) and \( C' \) vary drastically between the upper and lower spectra. The increase of the absorption \( C' \) in the concentrated sample indicates that it is associated with larger clusters, which is consistent with the theoretical spectra for \( n = 3 \) and 4 in Fig. 3 and with the experimental results in helium droplets.

The theoretical spectra in Fig. 3 also indicate that there are two fairly separated spectra in the trimer, but intense peaks that are approximately equal at 951.2 and 954.4 \, \text{cm}^{-1}. In contrast, the theoretical spectrum for the tetramer predicts a strong single absorption at 956.3 \, \text{cm}^{-1}. Although the calculated transition frequencies for the tetrahedral tetramer happen to agree with the observed absorptions \( C' \) and \( G \), the correspondence between the calculated and the observed spectra for the trimer is poor. The simplified model of the trimer and other unknown causes may be responsible for the disagreement. The absorption \( H \) may reasonably be associated with larger clusters than the tetramer since we observed a drastic increase of its intensity in extremely concentrated samples.

Before concluding the discussion, two brief comments will be made. One is the absorption of the triple degenerate bending mode \( (\nu_4) \) of \( \text{SF}_6 \). We have surveyed the absorption in the 608–618 \, \text{cm}^{-1} \) region corresponding to the \( \nu_4 \) mode. Figure 6 shows the spectrum observed for a sample in the closed-cell at a rather high ratio of 1.0 \times 10^{-4}.
that the overall splitting of the $\nu_4$ band is considerably smaller than that of the $\nu_3$ band. The splitting of two dimer transitions is estimated to be 2.5 cm$^{-1}$. Comparing this value with the splitting of 21.5 cm$^{-1}$ for the $\nu_3$ band, we can estimate the ratio of transition moments $\mu_{01}(\nu_4)/\mu_{01}(\nu_3)$ to be 0.34 by the use of Eqs. (5)–(7). The transition dipole moments in the gas phase are reported to be 0.388 and 0.116 debye for the $\nu_3$ and $\nu_4$ bands, respectively. From these data, the ratio of transition moments is calculated to be 0.30. The correspondence is fairly good considering the difference between the gas and solid phases.

The second point concerns the temperature dependence of the fine structure of the monomeric transition. The top panel of Fig. 4 shows an enlarged profile of the monomeric transition of SF$_6$ clusters. The sample was prepared by the closed-cell method.

FIG. 6. Spectrum of the $\nu_4$ vibrational transition of SF$_6$ clusters. The sample was prepared by the closed-cell method.

spectra of dimers and larger clusters are recorded and fairly well explained. The strong absorptions of the tetrahedral tetramer at about 957 cm$^{-1}$ observed in the present work have not been reported previously in studies using liquid helium droplets.

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