Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 28 Mar 2007.

To cite this article: R. Righini , P. R. Salvi & V. Schettino (1977): Coupled Phonon Modes and Infrared Band Shapes in Crystal SiF, Molecular Crystals and Liquid Crystals, 43:3-4, 223-234

To link to this article: http://dx.doi.org/10.1080/00268947708084669

Mol. Cryst. Liq. Cryst., 1977, Vol. 43, pp. 223–234

Printed in Holland

Coupled Phonon Modes and Infrared Band Shapes in Crystal SiF_4†

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(*Received October 28, 1976*)

The absorption intensities of combination bands in the infrared spectrum of crystal SiF_4 have been measured. One- and two-phonon energies and densities of states have been calculated with a dipole–dipole interaction potential. The contribution to absorption intensities due to non linear electric moments have been calculated. It is shown that most of the two-phonon infrared absorption is due to phonon–phonon coupling.

INTRODUCTION

The infrared and Raman spectra of the molecular crystal SiF_4 have been described in previous papers.[1–3] From the band profiles it was argued that most of the infrared absorption in the two quantum regions could be due to absorption processes where two vibrational quanta are excited at different lattice sites by a single photon. The mechanisms for two-phonon absorption have been discussed by Dows and Schettino[4] in a form suitable to molecular crystals and can be outlined as follows. A biexcitation can be caused directly by the radiation field through nonlinear terms in the expansion of the electric dipole moment or indirectly by means of an anharmonic coupling of an intense discrete state with the two-phonon continuum. On this basis general expressions for calculation of band intensities and shapes have been derived in the framework of exciton theory.

In previous papers[1–3] it was concluded from qualitative arguments that most of the two-phonon structure in crystal SiF_4 could arise from the direct excitation mechanism. We have now measured the absorption intensity of

† Supported by the Italian Consiglio Nazionale delle Ricerche.

the two-phonon bands observed in the infrared spectra and made quantitative comparison of calculated and measured intensities. This has led to changes in previous conclusions. It will be shown in the present paper that the absorption intensity in the two-phonon region is mainly due to the indirect mechanism. By adapting Fano's configuration interaction theory[5] to the SiF_4 crystal a satisfactory agreement between calculated and observed band shapes can be obtained.

METHOD OF CALCULATION

The calculations to be described have been performed in the harmonic approximation. Symmetrized wavefunctions describing the excitation of a quantum of the i-th degenerate component of the vibrational mode f propagating in a crystal of N unit cells are

$$|fi:\mathbf{k}> = N^{-1/2}\Phi_0 \sum_n \sigma_n^{fi} e^{i\mathbf{k}\cdot\mathbf{n}} \tag{1}$$

where $\Phi_0 = \Pi\varphi_n^0$ is the crystal ground state and $\sigma_n^{fi} = \varphi_n^{fi}/\varphi_n^0$ is the one site harmonic oscillator quotient function.[6] In this case the cell index n is sufficient to label the molecular wavefunction as the SiF_4 crystal contains only one molecule per unit cell.[7] States describing simultaneous excitation of two phonon f and g are defined in terms of the wave vector $\mathbf{k}_f$ and $\mathbf{k}_g$ of the two excitations

$$|fi, gj:\mathbf{k}_f, \mathbf{k}_g\rangle = N^*\Phi_0^{-1}|fi:\mathbf{k}_f\rangle|gj:\mathbf{k}_g\rangle \tag{2}$$

where the renormalization prevents from the two excitations being at the same site. The two-phonon states (2) may be expressed explicitly as a function of the total wave vector $\mathbf{k}_f + \mathbf{k}_g$ and lattice vector $\mathbf{R}_{nm} = \mathbf{n} - \mathbf{m}$

$$|fi, gj:\mathbf{k}_f, \mathbf{k}_g\rangle = \Phi_0[N(N-1)]^{-1/2} \sum_{n,m} \sigma_n^{fi}\sigma_m^{gj} e^{(\mathbf{k}_f+\mathbf{k}_g)\cdot\mathbf{m}} \times e^{i\mathbf{k}_f\cdot\mathbf{R}_{nm}}\cdot(1-\delta_{nm}) \tag{3}$$

In optical absorption the momentum conservation requires the total wave vector $\mathbf{k}_f + \mathbf{k}_g \simeq 0$ and therefore the only states of interest in the manifold (3) are, with $\mathbf{k}_f = -\mathbf{k}_g = \mathbf{k}$

$$|fi, gj:\mathbf{k}, -\mathbf{k}\rangle = \Phi_0[N(N-1)]^{-1/2} \sum_n \sum_m \sigma_n^{fi}\sigma_m^{gj} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}}(1-\delta_{nm}) \tag{3'}$$

$$= N^*\Phi_0^{-1}|fi:\mathbf{k}\rangle|gj:-\mathbf{k}\rangle$$

Calculation of energies of phonon states of the type (1) and (3′) have been performed in the harmonic limit and with neglect of intermode mixing by expanding the crystal potential in the local normal coordinates

$$2V = \sum_f \sum_{ni} \sum_{mj} F^f_{ni,mj} q^{fi}_n q^{fj}_m \tag{4}$$

In the dipole model the coefficients in the expansion (4) are different from zero only for normal modes ν_3 and ν_4 of species F_2 corresponding to $f = 3$ and 4, respectively, and are easily obtained from the general expressions of the interaction energy of a dipole array[8,9]

$$F^f_{ni,mj} = (\partial\mu/\partial q_f)^2 \mathbf{e}^{fi}_n \boldsymbol{T}_{nm} (\boldsymbol{E} + \boldsymbol{\alpha}\boldsymbol{T}_{nm})^{-1} \mathbf{e}^{fj}_m \tag{5}$$

where the transition dipole moment $(\partial\mu/\partial q_f)$ is known from experiment,[10] $\mathbf{e}$ is a unit vector in the direction of the transition dipole moment, $\boldsymbol{\alpha}$ is the static molecular polarizability and $\boldsymbol{T}$ is the field propagator.

Using the procedure described in (3) energies and crystal states for the one- and two-phonon states are evaluated. Energies, as a function of $\mathbf{k}$, of the one-phonon states for modes ν_3 and ν_4 are obtained by diagonalization of the 3×3 perturbation matrix H^f whose elements are

$$H^f_{ij}(\mathbf{k}) = \langle fi : \mathbf{k} | V | fj : \mathbf{k} \rangle = \sum_n e^{i\mathbf{k}\cdot(\mathbf{n}-\mathbf{m})} \langle \varphi^0_m \varphi^{fi}_n | F^f_{ni,mj} q^{fi}_n q^{fj}_m | \varphi^0_n \varphi^{fj}_m \rangle \tag{6}$$

and the crystal states are obtained from the appropriate eigenvectors

$$|\alpha f : \mathbf{k}\rangle = \sum_i B_{i\alpha}(\mathbf{k}) | fi : \mathbf{k}\rangle \qquad \alpha = 1, 2, 3 \tag{7}$$

The elements of the perturbation matrix for the two-phonon states (3′) can be expressed in terms of those for states (1), according to Craig and Schettino,[3] as follows

$$\langle fi, gj : \mathbf{k}, -\mathbf{k} | V | fk, gl : \mathbf{k}, -\mathbf{k}\rangle = \delta_{ik} H^q_{jl}(-\mathbf{k}) + \delta_{jl} H^f_{ik}(\mathbf{k}) \tag{8}$$

In our approximation, a simplification arises in the energy calculation of the two-phonon combination states of the triply degenerate modes ν_3 and ν_4 ($f = 3, 4$) with the infrared inactive modes ν_1 and ν_2 ($g = 1, 2$), because the first term on the right side of (8) vanishes. Correspondingly, the crystal wavefunctions for the two-phonon combination states are

$$|\alpha f, \beta g : \mathbf{k}, -\mathbf{k}\rangle = \sum_{ij} B_{i\alpha}(\mathbf{k}) \delta_{\beta j} | fi, gj : \mathbf{k}, -\mathbf{k}\rangle \tag{9}$$

and for the two-phonon overtone $2\nu_3$ and $2\nu_4$ are

$$|af, \beta f : \mathbf{k}, -\mathbf{k}\rangle = \sum_{ij} B_{j\alpha}(\mathbf{k})B_{i\beta}(-\mathbf{k})|\, fi,\, fj : \mathbf{k}, -\mathbf{k}\rangle \tag{10}$$

Evaluation of the transition probability from the ground state directly to the crystal states (9) and (10) involves the quadratic terms in the expansion in the phonon coordinates q_n^{fi} of the crystal dipole moment operator:

$$\mathbf{M} = \mathbf{M}_0 + \sum_{nfi} \mathbf{M}_n^{fi} q_n^{fi} + \tfrac{1}{2} \sum_{nfi} \sum_{mgj}{}' M_{nm}^{fi,gj} q_n^{fi} q_m^{gj} + \cdots \tag{11}$$

where the prime indicates that $nf \neq mg$.

By expressing the second order coefficients $\mathbf{M}_{nm}^{fi,gj}$ in terms of the molecular polarizability derivative $\boldsymbol{\alpha}'^{gj}$ and transition dipole moment $(\partial\mu/\partial q_f)$[4]

$$\mathbf{M}_{nm}^{fi,gj} = \boldsymbol{\alpha}'^{gj} \mathbf{T}_{nm} \mathbf{e}^{fi} (\partial\mu/\partial q_f) \tag{12}$$

the transition matrix element to crystal states (9) assume the form

$$\mathbf{M}_{\alpha\beta}^{fg} = \langle 0|M|\alpha f, \beta g : \mathbf{k}, -\mathbf{k}\rangle = \langle 0|q|f\rangle\langle 0|q|g\rangle \times \sum_i \sum_j B_{i\alpha}\delta_{\beta j} \sum_n \mathbf{M}_{nm}^{fi,gj} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}} \tag{13}$$

where $f = 3, 4$ and $g = 1, 2$, while in the case of states (10)

$$\mathbf{M}_{\alpha\beta}^{ff} = \langle 0|M|\alpha f, \beta f : \mathbf{k}, -\mathbf{k}\rangle = \langle 0|q|f\rangle^2 \sum_i \sum_j B_{j\alpha} B_{i\beta} \times \sum_n \mathbf{M}_{nm}^{fi,gj} e^{i\mathbf{k}\cdot\mathbf{R}_{nm}} \tag{14}$$

The total intensity of the two-phonon absorption is then calculated as the sum for all values of $\mathbf{k}$ of the squared modulated contributions (13) or (14)

$$I^{fg}(\omega) \propto \sum_{\alpha\beta} \sum_{\mathbf{k}} |M_{\alpha\beta}^{fg}|^2 \delta[\omega - \omega_{f\alpha}(\mathbf{k}) - \omega_{g\beta}(\mathbf{k})] \tag{15}$$

In the model adopted the two phonons are coupled directly to the electric field by the quadratic terms in the electric moment. From the form (12) of the coefficients in the electric moment expansion this mechanism may be pictured as follows. When an infrared active mode is excited at a given lattice site charges are induced at other lattice sites: vibrations of the induced charges can couple to the radiation field even if the second mode is not infrared active. Therefore this mechanism requires the two modes be one infrared and the other Raman active. From the range of values of the polarizability derivatives it is expected that intrinsic intensity in the two quantum region should be of order 10^{-3}–10^{-5} of the fundamentals.

RESULTS AND DISCUSSION

The broad structure of the combination modes $\nu_1 + \nu_3$, $\nu_2 + \nu_3$ and $\nu_1 + \nu_4$ and of the overtone $2\nu_3$ are shown in Figures 1–4. The density of states in these two quantum regions have been calculated with the method described in the preceding section using the experimental values of the parameter $(\partial\mu/\partial q_3)$, $(\partial\mu/\partial q_4)$ and α[10,11] and with an interaction radius of 30 Å. The present calculation differs from those described in previous notes[1,3] since the effect of mutual polarization of the molecular dipoles has been included in the intermolecular potential (5). This, as described in other cases,[12,13] has the effect of shifting the crystal levels to lower energies but does not affect to a greater extent the dispersion curves and the densities of states. The estimated LO–TO splittings are in good agreement with the experimental values showing that most of the dispersion of these phonons comes from dipole–dipole interaction.

In order to calculate the two-phonon intensities with the direct mechanism according to (15) the polarizability tensors for the modes ν_1, ν_2 and ν_3 are needed. By symmetry these have the form

$$\alpha'(1) \quad \begin{pmatrix} a & & \\ & a & \\ & & a \end{pmatrix} \qquad \alpha'(2) \quad \begin{pmatrix} b & & \\ & b & \\ & & -2b \end{pmatrix} \quad 3^{1/2}\begin{pmatrix} b & & \\ & -b & \\ & & 0 \end{pmatrix} \tag{16}$$

$$\alpha'(3) \quad \begin{pmatrix} & c & \\ c & & \\ & & \end{pmatrix}\begin{pmatrix} & & c \\ & & \\ c & & \end{pmatrix}\begin{pmatrix} & & \\ & & c \\ & c & \end{pmatrix}$$

Only the value of the parameter a is known from experiments[14] to be 3.15×10^{-5} c.g.s.u. To estimate the parameters b and c the intensity of the ν_3 and ν_2 Raman bands in the crystal have been measured relative to that of ν_1. The values obtained for b and c are 0.5×10^{-5} and 1.7×10^{-5} c.g.s.u., respectively. The calculated intensities are shown in Figures 1–4 in an arbitrary scale. It can be seen that the important features of the two-phonon spectra are reproduced in the calculated intensity pattern, and also in the two-phonon densities of states (see Refs. 1 and 3). However, we have measured the infrared intensity of two-phonon bands in the infrared spectrum of the crystal. The intensity measurements have been done adding to SiF_4 1% of sulfur hexafluoride as an internal standard. The intensity of the two-phonon bands have been then measured by comparison with that of the ν_6 fundamental of SF_6 which is well known.[15] From these results it is seen that the ratio I_{obs}/I_{calc} of

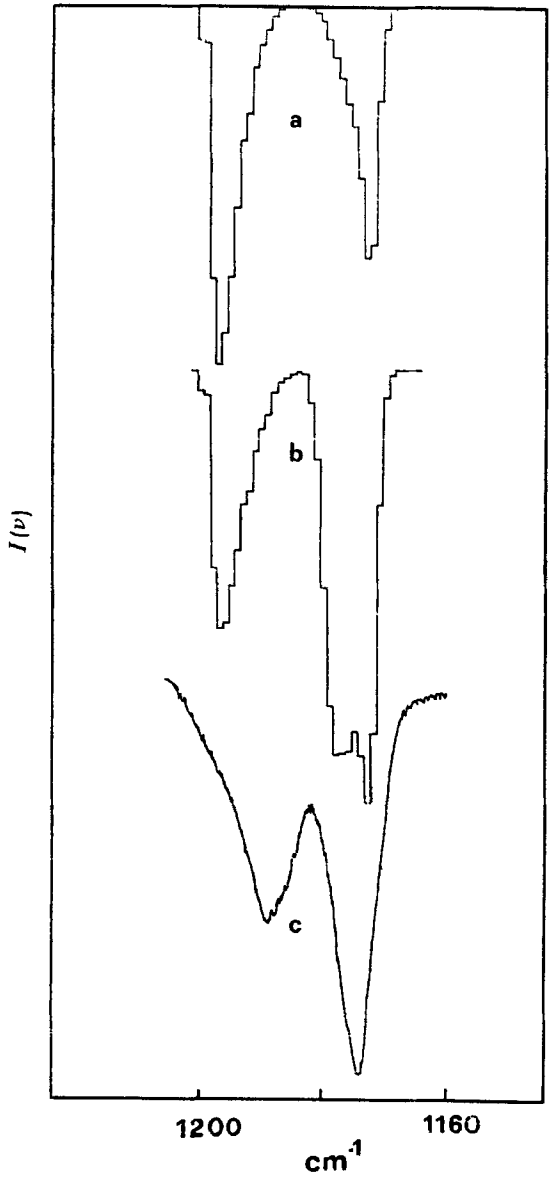

FIGURE 1 Infrared absorption in the $\nu_1 + \nu_4$ region of crystal SiF_4. a—absorption profile due to non-linear moments. b—absorption profile according to Fano's theory. c—experiment. Scale is arbitrary; for comparison of integrated areas see text.

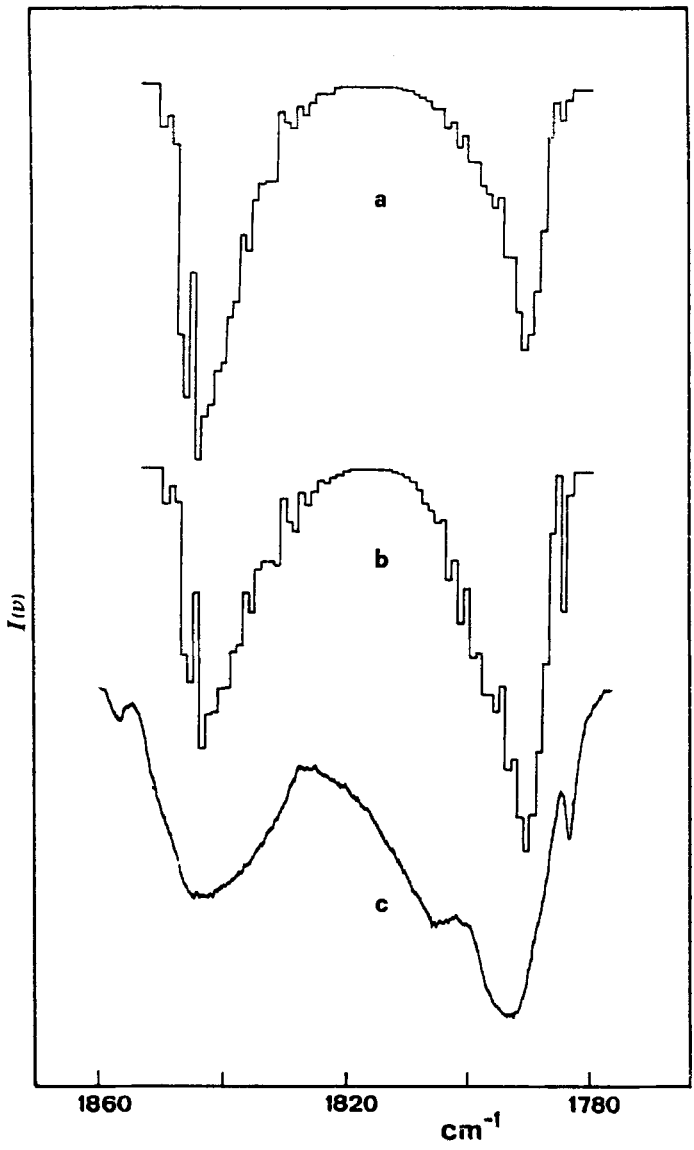

FIGURE 2 Infrared absorption in the $\nu_1 + \nu_3$ region of crystal SiF_4. a—absorption profile due to non-linear moments. b—absorption profile according to Fano's theory. c—experiment. Scale is arbitrary; for comparison of integrated areas see text.

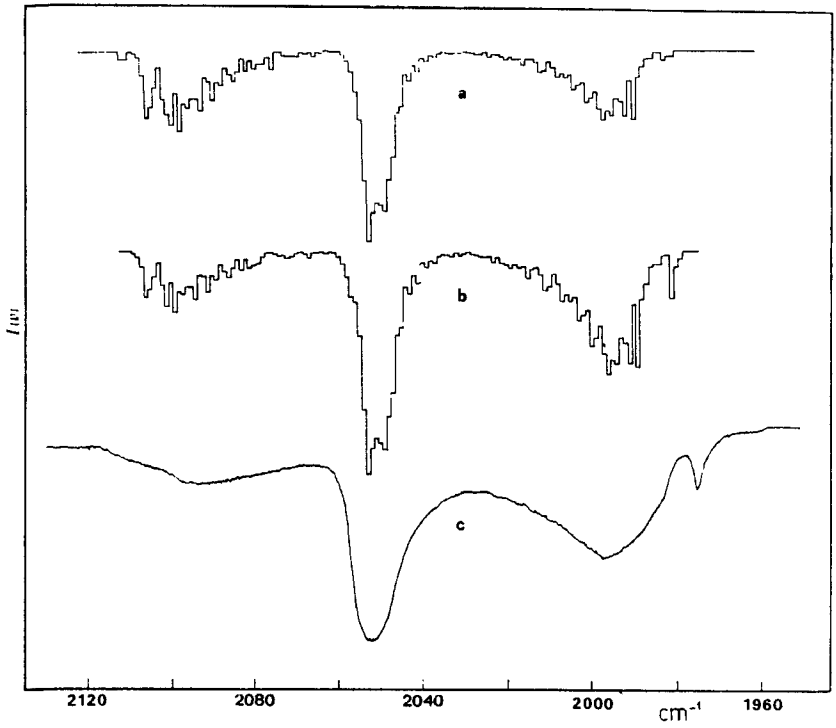

FIGURE 3 Infrared absorption in the $2\nu_3$ region of crystal SiF_4. a—absorption profile due to non-linear moments. b—absorption profile according to Fano's theory. c—experiment. Scale is arbitrary; for comparison of integrated areas see text.

the observed and calculated intensity for the modes $\nu_1 + \nu_3, 2\nu_3, \nu_1 + \nu_4$ and $\nu_2 + \nu_3$ is 70, 100, 300 and 450, respectively. The scatter of the results of various experiments for the $\nu_2 + \nu_3$ is very large and in general the entries reported are average values.

Regardless of the exactness of the above figures it must be concluded that the direct excitation mechanism through the nonlinear dipole moment accounts for only a small fraction of the observed absorption intensity. The main source of disagreement is most likely due to the fact that not all the states of interest have been considered in the manifold (3). In fact the factor $(1 - \delta_{nm})$ prevents the two quanta from being on the same site. These states excluded in (3) describe the excitation of the vibrational quanta on the same molecule and will hereafter be identified as "molecular combination" modes. Although these states are in principle two-phonon states it is more convenient to consider them separately from the manifold (3) for two reasons.

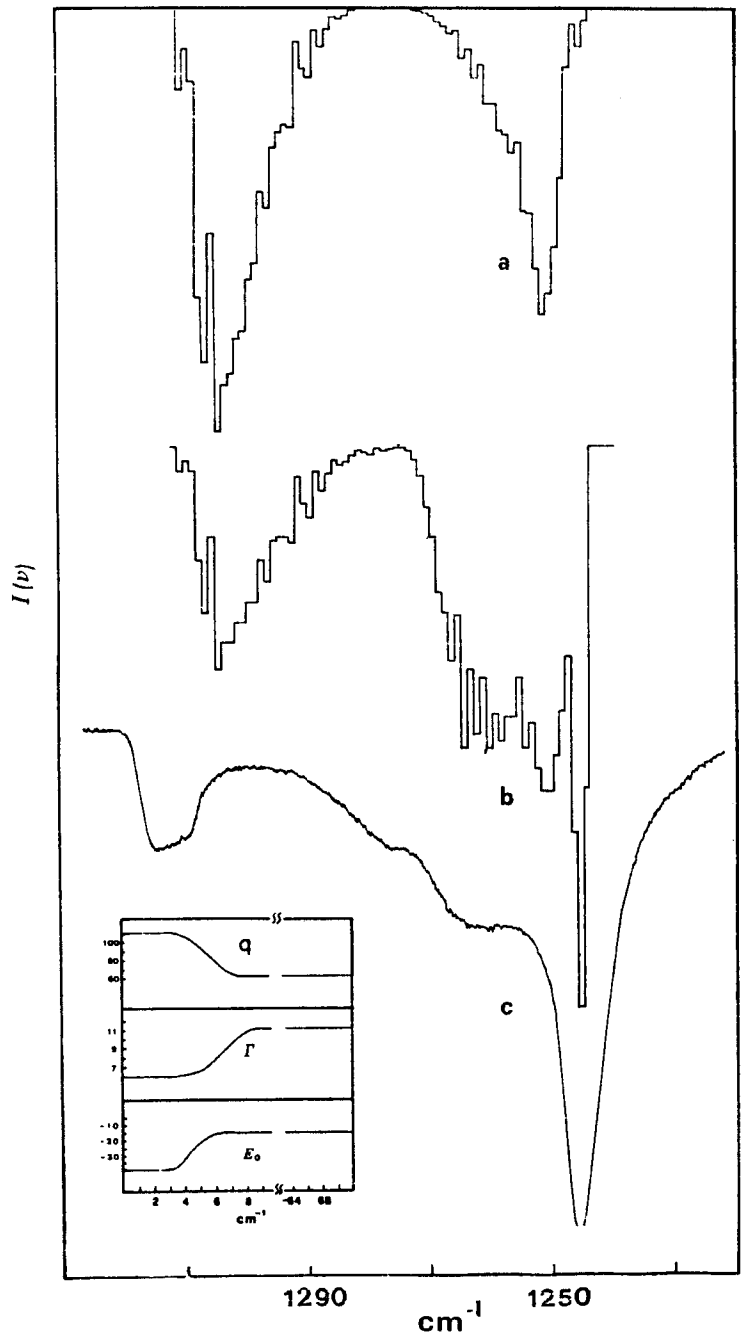

FIGURE 4 Infrared absorption in the $\nu_2 + \nu_3$ region of crystal SiF_4. a—absorption profile due to non-linear moments. b—absorption profile according to Fano's theory. c—experiment. Scale is arbitrary; for comparison of integrated areas see text. The values of the Fano's parameters are shown in the insert.

First, in contrast to states (3) the molecular combinations can be defined also in the gas phase and their energy is affected from the intramolecular anharmonicity. Secondly, although in the particular cases of combination of two different modes the molecular combination modes are simply obtained from (3) by substituting the factor $(1 - \delta_{nm})$ with δ_{nm}, it is not always necessarily so. This happens for instance in the case of the molecular overtone $2\nu_3$, as it can be seen from the form of the Hermite polynomials. Molecular combination states are then more properly expressed as

$$|(f + g)i, \mathbf{k}\rangle = N^{-1/2}\Phi_0 \sum_n \sigma_n^{(f+g)i} e^{i\mathbf{k}\cdot\mathbf{n}} \tag{17}$$

It is understood that only the states (17) with $\mathbf{k} = 0$ are of interest in optical absorption. Therefore, as far as the present experiment is concerned, the molecular combination is to be considered as a sharp state which has associated a relatively strong transition dipole moment, since these combination modes give prominent bands in the infrared spectrum of the gas.[16] The infrared activity of combinational modes is assumed by the nonlinear terms in the dipole moment, and more exactly by the terms excluded in the expansion (11) by the prime on the second summation.

From the assumed form of the crystal wavefunctions (3) and (17) it is seen that there is a harmonic coupling between the molecular combination and the two-phonon states and, in addition, an anharmonic coupling can be effective. This is a type of intermolecular Fermi resonance that will redistribute the intensity of the molecular combination tones through the two-phonon continua. Since the two-phonon intensity due to direct mechanism is only a very small fraction of the total intensity it is legitimate to assume that the two-phonon absorption is essentially due to the molecular combination which is diluted into the continuum by the coupling discussed above. The peculiarities of the present problem are further specified by noting that the intramolecular anharmonicity in SiF_4 is small[16] and therefore the molecular combination falls into the continuum of the two-phonon states (3) toward its lower frequency limit.

A theory of configuration interaction between overlapping sharp and diffuse states has been developed by Fano[5] and has been successfully applied in the analysis of the electronic[17] and vibrational[18,19] spectra. This formalism is amenable for application to the present case.

According to Fano we define a sharp state φ_0 (corresponding to our molecular combination) and a continuum of states φ_E, corresponding to the two-phonon states (3), which interact through a perturbation Hamiltonian H' such that the perturbation matrix elements are

$$\langle \varphi_0 | H' | \varphi_E \rangle = V_E \tag{18}$$

By diagonalization of the perturbation matrix, new hybrid states of the form

$$\psi_E = a\varphi_0 + \int b_E \varphi_E \, dE \tag{19}$$

are produced, where $|a|^2$ and $|b|^2$ give a measure of the mixing of the initial configurations. We may express the transition probability from the ground state to the perturbed states ψ_E as a function of that to the unperturbed states φ_E as follows

$$\frac{|\langle 0|\mu|\psi_E\rangle|^2}{|\langle 0|\mu|\varphi_E\rangle|^2} = \frac{[q + 2(E - E_0)/\Gamma]^2}{1 + [2(E - E_0)/\Gamma]^2} \tag{20}$$

where E_0 is the resonance energy of the sharp state ψ^* after perturbation, h/Γ is the mean lifetime of the discrete state φ_0 with respect to the decay into the continuum and q is a parameter such that $q^2\Gamma$ is a measure of the strength of the transition to ψ^* relative to that to the states of the continuum. In application of (20) to the two-phonon bands in SiF_4 we require an intensity enhancement to reproduce the experimental observation, and, in addition, the peculiarity of the present situation is that the continuum has a structure and an intrinsic intensity. Although in Fano's theory the three parameters q, E_0 and Γ appearing in (20) are in principle different for each state of the continuum, in previous applications[17–19] it has been assumed that they vary very slowly in the region of interest and therefore have been assumed to be constant. With this assumption it is always possible to reproduce the integrated band intensity but, as to the band profile, this assumption gives a satisfactory result only for the $\nu_1 + \nu_3$ region as shown in Figure 1. In all other cases it is not possible to reproduce the peculiar sharp peak observed in the low frequency side of the two-phonon bands. It is possible to circumvent this difficulty assuming that the parameters q, E_0 and Γ are not constant in all the region of interest. In the case of $\nu_1 + \nu_3$ and $2\nu_3$ satisfactory results are obtained assuming two different sets of parameters, one for a small range around the discrete state and another for the remaining two-phonon states. The results obtained are reported in Table I. Even in this approximation it is not possible to obtain a satisfactory result for the $\nu_2 + \nu_3$ region, where the low frequency sharp peak dominates over the intensity of the continuum. In this case it is possible to obtain a satisfactory result only assuming that the parameters have a continous variation with increasing energy separation from the discrete state. The result is shown in Figure 4.

On the basis of the intensity measurements and calculations described in the present paper it can be concluded that the states giving rise to the two-phonon absorption in SiF_4 crystal are an hybridization of molecular combinations and proper two-phonon states where the two quanta are

TABLE I

Fano's parameters in Eq. 20 for combination bands of crystal SiF_4.

	$\nu_1 + \nu_4$	$\nu_1 + \nu_3$		$2\nu_3$	
		a	*b*	*a*	*b*
E_0	−4	−30	−12	−59	−45
Γ	6	2	35	2.5	135
q	50	14	12	20	12

E_0 and Γ are in cm^{-1}. *a* and *b* refer to parameter values in the vicinity and far away from the discrete state (see text).

excited on different molecules. The bulk of intensity in the two-phonon regions derives from excitation of two quanta on a single molecule and subsequent stealing of intensity into the two-phonon continuum through intermolecular coupling. The peaks in the calculated band profiles are considerably sharper than observed experimentally. This is due to the assumption that the two-phonon states (3) are in the form of delta functions. If these states are allowed to have an intrinsic width the agreement would be improved.

References

1. V. Schettino, in *Lattice Dynamics and Intermolecular Forces*, Ed. S. Califano, Academic Press, London, 1975.
2. V. Schettino, *Chem. Phys. Letters*, **18**, 535 (1973).
3. D. P. Craig and V. Schettino, *Chem. Phys. Letters*, **23**, 315 (1973).
4. D. A. Dows and V. Schettino, *J. Chem. Phys.*, **58**, 5009 (1973).
5. U. Fano. *Phys. Rev.*, **124**, 1866 (1961).
6. D. P. Craig, *Advances in Chemical Physics*, Ed. I. Prigogine, VIII, 27 (1965).
7. M. Atoji and W. N. Lipscomb, *Acta Cryst.*, **7**, 597 (1954).
8. M. Mandel and P. Mazur, *Physica*, **24**, 116 (1958).
9. J. Decius, *J. Chem. Phys.*, **49**, 1387 (1968).
10. P. N. Schatz and D. F. Hornig, *J. Chem. Phys.*, **21**, 1516 (1953).
11. Landolt-Börnstein, *Zahlenwert und Functionen*, Springer (1951), Vol. I, part 3.
12. D. A. Dows and V. Schettino, *Spectrochim. Acta*, **30A**, 1451 (1974).
13. V. Schettino and P. R. Salvi, *Spectrochim. Acta*, **31A**, 411 (1975).
14. W. Murphy, W. Holzer, and H. J. Bernstein, *Appl. Spectr.*, **23**, 211 (1969).
15. D. A. Dows and G. M. Wieder, *Spectrochim. Acta*, **18**, 1567 (1962).
16. J. Heicklen and V. Knight, *Spectrochim. Acta*, **20**, 295 (1964).
17. M. D. Sturge, H. J. Guggenheim, and M. H. L. Price, *Phys. Rev.*, **B2**, 2459 (1970).
18. D. L. Rousseau and S. P. S. Porto, *Phys. Rev. Letters*, **20**, 1354 (1968).
19. J. F. Scott, *Phys. Rev. Letters*, **24**, 1107 (1970).