Dispersed fluorescence spectroscopy of the SiCN $A^2\Delta - X^2\Pi$ system: Observation of some vibrational levels with chaotic characteristics

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Observation of some vibrational levels with chaotic characteristics in view of the two-dimensional harmonic oscillator (2D-HO) basis which is characterized by the vibronic labels of the levels are meaningless, and the vibronic assignments for the levels, but just vibronically labeled, referring the largest component in their vectors. (To emphasize this situation, we do not use the word “assignment,” but prefer to use “label” as the meaning of just “label,” but not “assign,” throughout this paper.) The latter shows that the vibronic labels of the levels are meaningless, and the $P$ quantum number and the order of their eigen states in the $P$ matrix block derived in the numerical analysis only characterize the vibronic levels. Comparing the constants obtained for all of the interactions with those of species showing Sears resonance and studied previously, it is found that none of them are strong, but are moderate. It is thus concluded that the chaotic appearance is not derived by any strong interaction, but is induced by complex and accidental proximities of the vibronic levels caused by the moderate interactions. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4967251]
of the electronic transition. In addition to the cold bands, vibrationally hot bands have been also recognized, though they are much weaker than the cold bands. The rotational structure of the hot bands, $A(01′0) \, ^3\Phi - \tilde{X}(01′0) \, ^3\Delta$ and $A(01′0) \, ^5\Pi - \tilde{X}(01′0) \, ^5\Sigma^−\), has been analyzed, and it was reported that the $l$-basis is better to describe the rotational intensity structure of the bands than the $K$-basis.\textsuperscript{11}

Contrary to the hot bands, the analysis of the cold bands was not straightforward due to two problems in the $\tilde{X} \, ^2\Pi$ state; one had been on the SO constant, $A$. The problem on $A$ is that the value derived in our rotational analyses of the optical spectra is about twice of that derived from the mm-wave spectra.\textsuperscript{3,4} For this problem, we have performed combined analysis with the mm-wave and our optical information, and have shown that there are no contradictions between our constant and the mm-wave spectra.\textsuperscript{12} The optical spectra can provide information on the relative energy between the $P'' = \frac{4}{2}$ and $\frac{7}{2}$ spin sub-levels, because those consist of four vibronic transitions, $P'' = \frac{4}{2}$ and $\frac{7}{2}$–$P'' = \frac{1}{2}$ and $P'' = \frac{3}{2}$ and $\frac{5}{2}$–$P'' = \frac{1}{2}$, while mm-wave spectra only give information within one spin sub-level, i.e., the rotational transition within the same $P''$ components. It is thought that the unreliability of $A$ in the mm-wave spectra causes the insufficient information. The other problem has been in the vibrational structure of the $\tilde{X} \, ^2\Pi$ state; we have assigned the vibronic bands in the SVL DF spectra, but the analysis adopting a procedure derived from perturbation treatment on R–T had not succeeded, because there were unexpectedly large deviations on the analysis. There had been two possibilities for the unsucces; one was wrong assignments and the other was wrong analysis procedure. Our assignments are in relatively good correspondence with those predicted from the computational work.\textsuperscript{10} Thus, we tried to analyze the structure by a method adapting numerical diagonalization procedure.\textsuperscript{13} In the present paper, we have described the numerical diagonalization analysis of the vibrational structure of the $\tilde{X} \, ^2\Pi$ state observed in the DF spectra.

II. EXPERIMENT

The experimental details have been given in our previous SiCN study on the cold bands.\textsuperscript{11,12} Applying laser ablation technique, the SiCN radicals were generated in supersonic free jet expansions. The metallic surface of a silicon rod was ablated using 2nd harmonics of a Nd\textsuperscript{3+} YAG laser, and Si in the radical would be supplied from the Si ablated. Decomposition products of acetonitrile in plasma generated by the ablation would be the source for CN. The second harmonics of a pulsed dye laser was used to detect the LIF signals. The energy resolution of the UV light source was ~0.3 cm\textsuperscript{−1}. The absolute frequency of the light source was achieved from opto-galvanic signals of Ne for the red fundamental laser, whose signals are simultaneously recorded with the SiCN spectrum. For the measurement of the dispersed fluorescence (DF) spectrum, a monochromator with 500 mm focal length was used. The line width resolution of the DF spectrum was about 20 cm\textsuperscript{−1}, and the peak accuracy would be less than ±5 cm\textsuperscript{−1}. The spectral settings of the monochromator were established using the Hg atomic lines.

To measure the strength of the excitation light source scattered into the monochromator, spectra measured at the experimental condition without the ablation laser were recorded just after the DF spectrum measurements. The LIF signals were calibrated using power of the monitoring UV light source in each shot through the experiment.

Calculation was performed on a desktop server with AlphaPC 164LX mother board, Compaq DEC, with a 64 bit CPU, DEC Alpha 21164A. The programs were coded in FORTRAN language and were compiled by DEC or gnu FORTRAN. The numerical calculation package LAPACK was used for the diagonalization subroutine.

III. RESULTS

A. SVL DF spectra

The LIF of the $A \, ^2\Delta - \tilde{X} \, ^2\Pi$ transition of SiCN has been observed in the UV region, and the LIF excitation spectrum has been measured. Figure 1 shows the survey spectrum. Although this has been published in our previous reports,\textsuperscript{11,12} additional information has been added. In the survey spectrum, six vibronic bands with relatively strong intensity have been assigned as cold bands of the electronic spectrum,\textsuperscript{11} and three with relatively weak intensity have been assigned as vibrationally hot bands.\textsuperscript{11} The rotational structures of the cold bands have been analyzed, and agreements between the molecular constants, except the spin-orbit constant, $A$, determined for the lower electronic state and those reported on the rotational spectroscopy\textsuperscript{3,4} have confirmed the assignment of the spectral species.\textsuperscript{12}

Two bands at 29 327 and 29 195 cm\textsuperscript{−1} in the six cold bands have been attributed to the transitions from the two electron spin components, $P'' (=\Omega'') = \frac{1}{2}$ and $\frac{3}{2}$, respectively, of the $0^0$ band. The SVL DF spectra of the two vibronic bands were reported in our previous reports,\textsuperscript{12} and are shown in FIG. 1.
some of them had not been straightforward as described in Subsections III B and III C.

The other four vibronic bands in the six cold bands have been attributed to the transitions to the vibronic levels affected by Fermi interaction between $2\nu_3$ and $\nu_1$ in the $\tilde{A}^2\Sigma^+$ state, and they are categorized into two pairs: bands at 29934 and 29802 cm$^{-1}$ and those at 29995 and 29864 cm$^{-1}$, which were labeled as $\alpha$ and $\beta$ bands, respectively, as shown in Fig. 1. The rotational structures of the $\alpha$ and $\beta$ bands have been analyzed as $2\Sigma^+ - 2\Pi$ transition. The stronger band in each pair (the 29934 and 29995 cm$^{-1}$ bands for $\alpha$ and $\beta$, respectively) is attributed to the transition from the lower electron spin sub-level, $P'' = \frac{1}{2}$, and the weaker one in each pair (the 29802 and 29864 cm$^{-1}$ bands for $\alpha$ and $\beta$, respectively) is attributed to that from the higher component, $P'' = \frac{3}{2}$. Figures 3 and 4 show the SVL DF spectra from each component of the Fermi resonance. Spectra (b) and (c) in Figs. 3 and 4 are the SVL DF spectra obtained by the excitation of the $Q_1$ band-head of the $\alpha$ and $\beta$ bands, respectively, and spectra (c) in the figures are those of the $Q_2$ band-head of $\alpha$ and $\beta$, respectively. The vibronic structures of the two SVL DF spectra from the lower spin component of the $\alpha$ and $\beta$ bands have been compared in our previous report, and remarkable $\nu_3$ progressions on the $2\nu_2$ bending level are recognized, which is one of the experimental evidences for the Fermi resonance in the upper vibronic levels of the $\alpha$ and $\beta$ bands. In addition to the major $\nu_3$ progressions, there are weak but considerable vibronic bands in the spectra. As same with the SVL DF spectra from the vibrationless levels mentioned above, they are attributed to the bands fluorescent to the level with characteristics of the $\nu_2$ bending mode as described in Subsections III B and III C.

The three hot bands in the survey spectrum, Fig. 1, are categorized into two: one is a pair of the 29421 and 29302 cm$^{-1}$ bands and the other is the 29451 cm$^{-1}$ band alone. On the basis of the rotational analyses, the former and latter bands are attributed to the $\tilde{A} (011^0) 2\Phi - \tilde{X} (011^0) 2\Pi$ and $\tilde{A} (011^0) 2\Pi - \tilde{X} (011^0) \mu 2\Sigma^-$ vibronic transitions, respectively. Figure 5 shows the SVL DF spectra of the two hot bands at 29421 and 29451 cm$^{-1}$. The SVL DF spectra have been reported in our previous report, but different from the figure published, the horizontal scale is shifted to show absolute energy of the levels, because the origins of the spectra of the hot bands are the level energies of (011$^0$) $2\Delta_2^+$ and (011$^0$) $\mu 2\Sigma^-$ for spectra (b) and (c), respectively. Spectra (b) and (c) are those fluorescent to the $\tilde{A} (011^0)$ $4\Phi_2^+$ and $2\Pi_2^+$ levels, respectively. The spectrum from the $4\Phi_2^+$ level has two $3\nu_3$ progressions, the spacing between which is close to the spin splitting, $\sim$ 140 cm$^{-1}$, in the $2\Pi_2^+$ state, and the vibronic structure of spectrum (b) is very similar to that of spectrum (a) which is the same as spectrum (a) in Fig. 2, i.e., that of the SVL DF spectrum from the $P' = \frac{3}{2}$ component of the 0$^0_2$ band. In contrast, spectrum (c) of the $2\Pi_2^+$ level also has the two $3\nu_3$ progressions, but the spacing between the two progressions is wider than that of the $4\Phi_2^+$ spectrum (b), and it has been concluded for spectrum (c) that the spacing corresponds to that between the two $\Sigma$ levels, $\tilde{X} (011^0) \mu 2\Sigma^-$ and $\kappa 2\Sigma^+$ (11). (The lower and higher R-T pair are labeled $\mu$ and $\kappa$, respectively, by Hougen.) Besides the major $\nu_3$ progressions assigned.

Fig. 2 with additional information. Because spectra (a) and (b) in Fig. 2 are obtained by the excitation of the band-head of the $Q_1$ and $Q_2$ branches, respectively, they are DF from the $P'' = \frac{1}{2}$ and $= \frac{1}{2}$ levels, i.e., the $\tilde{A}$ (000$^0$) $2\Delta_2^+$ and $2\Delta_2^-$ levels, respectively. Then the transitions to the $P'' = \frac{3}{2}$ and $= \frac{3}{2}$ levels are observed as the major structure in the SVL DF spectra (a) and (b) in Fig. 2, respectively, because of the $\Delta \Sigma = 0$ selection rule under Hund’s case a limit. In spectra (a) and (b) in Fig. 2, the bands to $P'' = \frac{3}{2}$ and $= \frac{1}{2}$, respectively, are also observed, but weakly. As described in our previous work, the progression of the $\nu_3$ Si–CN and the $\nu_1$ C–N stretching modes appeared as the major vibronic structure in the spectra. In the spectra, additional vibronic bands, such as those indicated by arrows, are recognized weakly but considerably. They are attributed to vibronic bands fluorescent to vibronic levels with characteristics of the $\nu_2$ bending mode, but assignments for

FIG. 2. The LIF dispersed spectra obtained by the excitation of the 0$^0_2$ band, $P'' = \frac{1}{2}$ (a) and $= \frac{1}{2}$ (b), which are 29327 and 29195 cm$^{-1}$ bands, respectively, in the survey spectrum, Fig. 1. Spectrum (b) is put on the position slid about the value of the $A$ constant of the $\tilde{X}^2\Pi$ state each other, and thus the structures corresponded by broken lines indicate the same terminal vibronic levels. The broken lines show the stretching progressions, $3\nu_2$ and $\nu_2$, where the (000$^0$) $2\Pi_2^+$ level is identically labeled (see Subsection III C 3 in the text).

Dotted lines mean that the band marked by the corresponding broken line is not observed on the spectrum. Arrows indicate bands with the lower vibronic levels assigned on the present numerical analysis. Asterisks (*) indicate bands with large deviation on the analysis. The horizontal axis of each spectrum represents relative energy from the excitation energy. As a reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without the ablation laser were inserted. The peak positions and base levels of the signal inserted are shifted, and the actual positions and levels are 0 cm$^{-1}$ and the same with the signal back ground levels, respectively.
The LIF DF spectra obtained by the excitation of the levels, respectively.

To analyze the vibronic structure with the \( \nu_2 \) bending mode, i.e., the structure affected by the R-T effect, there are some methods, such as analysis adopting the formulation derived from perturbation approach and adopting numerical direct diagonalization of a matrix equation with a vibronic Hamiltonian. The vibronic structure derived from the vibronic bands assigned was initially analyzed adopting the method derived from the perturbation treatment, but it had not succeeded. One of the findings for the unsucces is electron spin splitting at the two R-T components, \( \mu \) and \( \kappa \). According to the perturbation treatment on the R-T and SO interactions, the same splitting for the two components, \( \mu \) and \( \kappa \), is expected, though the observed splittings show unexpectedly large difference in the \( \tilde{X}^\Pi \) state of SiCN, for example, 18 and 30 cm\(^{-1}\) for (020) \( \mu \) and \( \tilde{X}^\Pi \) respectively. In addition to the spin splitting problem, we have the other problem, i.e., we could not assign the weak bands in the observed spectra, such as the bands marked by arrows in the spectra in Figs. 2–5. At this stage, it is said that the vibrational structure of the \( \tilde{X}^\Pi \) state contains a chaotic structure in general meaning. We then gave up the perturbation approach, and took the method adopting numerical direct diagonalization described in Subsection III B.

**B. Analysis of the vibronic structure**

We made two kinds of computer programs to analyze the \( \nu_2 \) bending vibronic structure of the \( \tilde{X}^\Pi \) state: one is diagonalized in \( K \) blocks and another is done in \( P \) blocks.
At the first step, a code for the vibronic Hamiltonian including only the R-T term as an off-diagonal element was programmed, according to Gauyacq and Jungen.\textsuperscript{13} As the basis function for the vibronic Hamiltonian, product of electronic and vibrational wave-functions, $|\Lambda; v_2, l\rangle = |\Lambda\rangle|v_2, l\rangle$, was adopted, where $|\Lambda\rangle$ and $|v_2, l\rangle$ are wave-functions of the electronic one with $\Lambda = \pm 1$ and of the vibrational one of the two-dimensional harmonic oscillator (2D-HO), respectively. As shown in “II block” of Table 1 in Ref. 13, the basis functions of each $v_2$ consist of $\Lambda = \pm 1$ pair, and one of the pair of the lowest $v_2$ in each $K$ block except $\Sigma (K = 0)$ does not exist. Because we took positive $K$ space as the basis function (in the present vibronic discussion, both $K$ with plus and minus sign, $\pm |K|$, are degenerate completely, and then it is enough to consider one of the two $K$ spaces only), the lowest row and lowest column, i.e., the $\Lambda = -1$ element, was deleted in the present analysis, while Gauyacq and Jungen deleted the second row and second column, i.e., the $\Lambda = +1$ element, because of their choice of the negative $K$ space.\textsuperscript{13} The rest of the pair of the lowest $v_2$ in each $K$ constitutes a “unique level” defined by Jungen and Merer,\textsuperscript{17} which is much less effective for the R-T interaction than the other levels with $K \neq 0$ (so-called non-unique levels).\textsuperscript{14} The Hamiltonian matrix at the present stage is fundamentally the same with “II block” in Table 1 by Gauyacq and Jungen.\textsuperscript{13} The diagonal term of the vibronic Hamiltonian matrix only has the first $\omega_2$ term of the right-hand side in Eq. (1), and thus the vibronic Hamiltonian is as follows:

\[
H_{ee}^{\text{1st}} = H_{\text{dia}}^{\omega_2} + H_{\text{RT}},
\]

where $H_{\text{RT}}$ is the Hamiltonian for R-T. Using the R-T parameter, $\epsilon$, and the bending frequency, $\omega_2$, and using the matrix elements of the 2D-HO\textsuperscript{18-20} with the phase defined by Di Lauro and Mills,\textsuperscript{21} the off-diagonal matrix elements for the first step Hamiltonian were evaluated, and our matrix elements were confirmed with references, such as Frye and Sears\textsuperscript{22} and Smith \textit{et al.}\textsuperscript{23} The matrices in our code were constructed in each $K$. Our calculation code completely reproduces the same results on the numerical calculation for the $\tilde{X}^3\Pi\ CO_2$ system with $g_K = 0$ and $g_4 = 0$ by Gauyacq and Jungen,\textsuperscript{15} which is the leftmost column of their Table 2 (where $g_4$ is $g_{22}$ in their notation, and $g_K$ and $g_4$ will be described in the next paragraph).

At the second step, the anharmonic and Herzberg-Teller (H-T) terms were included into the first step Hamiltonian matrix having only the R-T term,

\[
H_{ee}^{\text{2nd}} = H_{ee}^{\text{1st}} + H_{\text{anh}}^{\omega_2} + H_{\text{HT}},
\]

where $H_{\text{anh}}^{\omega_2}$ and $H_{\text{HT}}$ are Hamiltonians for the anharmonic and H-T terms, respectively. The anharmonic term, $H_{\text{anh}}^{\omega_2}$, was introduced into the matrix as the $g_4$ and $g_4$ terms defined by Brown and Jørgensen.\textsuperscript{18,24} The diagonal elements of the $g_4$ and $g_4$ anharmonic terms were added into those of the first step, and the off-diagonal terms were also added into the positions of the “diagonal block” in the matrix shown in Fig. 2 by Smith \textit{et al.}\textsuperscript{23} The basis function is the same with that used in the first step. The matrix elements were evaluated and were confirmed with references, such as Frye and Sears\textsuperscript{22} and Smith

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{The LIF DF spectra obtained by the excitation of the 0\textsubscript{1} band, $P'' = 1/2$ (a), and the two 2\textsubscript{1} hot bands, 29,421 (b) and 29,451 cm\textsuperscript{-1} bands (c), in the survey spectrum, Fig. 1. Asterisks (+) indicate bands with large deviation. Spectra (b) and (c) are put on the position slid the lower vibronic level energies of the hot bands, (0\textsuperscript{1}0\textsuperscript{1}) $\Delta \tilde{2} \Sigma$ and (0\textsuperscript{1}0\textsuperscript{1}) $\mu \Sigma^\alpha$ of the $X \tilde{X}^3\Pi$ state (cf. Fig. 2 in our previous paper\textsuperscript{15}). The horizontal axis of each spectrum represents relative energy from the excitation energy. The broken lines show the stretching progressions, $3_\alpha$ and $1_\alpha$, on (0\textsuperscript{1}0\textsuperscript{1}) $\Pi$ or (0\textsuperscript{1}0\textsuperscript{1}) $\Delta \tilde{2} \Sigma$ and $\mu \Sigma^\alpha$ of (a) or (b) and (c), respectively. Arrows indicate bands with the lower vibronic levels assigned on the present numerical analysis. As a reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator, the spectra measured at the experimental condition without reference for the strength of the excitation light source scattered into the monochromator.}
\end{figure}
et al.23 The H-T term, \( H_{\text{HT}} \), was introduced as the \( g_K \) term found by Brown,25 though Gauyacq and Jungen evaluated this term by direct diagonalization.13 The matrix elements of the \( g_K \) term were evaluated and were confirmed.22,23,25 Our code completely reproduces the same results on the numerical calculations, Table 2 in Gauyacq and Jungen13 with \( g_K \neq 0 \) and \( g_4 \neq g_2 \neq 0 \) (where \( g_4 \) is \( g_{2''} \) in their notation).

At the third step, the spin–orbit (SO) interaction was added into the diagonal matrix elements of each \( K \) block. This is achieved by adding the last term of Eq. (1) into the diagonal element at the second step (including the anharmonic, \( g_4 \), and H-T, \( g_K \), terms), and thus the two matrices corresponding to \( \Sigma = +\frac{1}{2} \) and \( =-\frac{1}{2} \) components were obtained separately,

\[
H_{\text{ev}}^{3\text{rd}} = H_{\text{ev}}^{2\text{nd}} + H_{\text{SO}}
\]

and they also correspond to \( P = K + \frac{1}{2} \) and \( =K-\frac{1}{2}, \) respectively, and to basis functions, \( |K; \Lambda; \Sigma; v_2, l, \rangle = |\Lambda\rangle |\Sigma\rangle = \pm \frac{1}{2} |K; v_2, l\rangle \) and \( |\Lambda\rangle |\Sigma\rangle = \mp \frac{1}{2} |K; v_2, l\rangle \), respectively, where \( |\Lambda\rangle \) and \( |K; v_2, l\rangle \) are the same with those mentioned at the first step, and \( |\Sigma\rangle \) is wave-function of the electron spin. Our code completely reproduces the same results on the numerical calculations for the \( \tilde{X} \) \( ^2\Pi \) SICD system with \( \alpha = 0, \)23 where the Fermi resonance is included in the calculation, but the constants for the resonance are zero. At the present third stage, the code to analyze vibronic structure of pure bending mode with R-T on a \( ^2\Pi \) electronic state, including anharmonic and H-T terms, was established.

In the fourth step, the Fermi resonance was considered. The diagonal block with \( K \) (or \( P \)) with all of the terms of Eq. (1), i.e., \( H_{\text{dia}} \), as the diagonal elements is almost the same as that of the third step,

\[
H_{\text{ev}}^{4\text{th}} = H_{\text{dia}} + H_{\text{RT}} + H_{\text{SO}} + H_{\text{HT}} + H_{\text{Fermi}},
\]

where \( H_{\text{Fermi}} \) is the Hamiltonian for the Fermi resonance, and the resonance is only effective in the “off-diagonal block” between the \( K \) (or \( P \)) blocks with \( \Delta K = \pm 1 \), as shown in Fig. 2 by Smith et al.23 Using parameters, \( W_1 \) and \( W_2 \), introduced by Hougen26 and using the basis set of the 2D-HO, \( |K; \Lambda; \Sigma; v_2, l, \rangle = |\Lambda\rangle |\Sigma\rangle |K; v_2, l\rangle v_3 \), where \( v_3 \) is the one-dimensional harmonic oscillator wavefunction of the \( v_3 \) mode, the matrix elements of the Fermi interaction were evaluated, and our elements were confirmed with references, such as Hougen,26 Frye and Sears,22 and Smith et al.23 The code was checked using the CO \( \tilde{X} \) \( ^2\Pi \) system by Frye and Sears22 and SiCH \( \tilde{X} \) \( ^2\Pi \) by Smith et al.23 Up to the fourth stage, there is no distinction for our two programs, diagonalized in \( K \) or \( P \) block, and our code diagonalized in \( K \) with each \( \Sigma \) (SO component) is established. After this stage, the second-order interaction combined with the H-T and SO interactions, so-called Sears resonance, was included into the Hamiltonian at the present fourth stage. It should be noticed that Sears resonance mixes \( \Delta K = \pm 1 \) levels and, after including the resonance, \( K \) is not a good quantum number anymore, but \( P \) is.

Northrup and Sears proposed Sears resonance to understand a local perturbation between the \( \tilde{X} \) (01 \(^1\) \( ^0 \)) \( ^2\Delta_\frac{1}{2} \) and (02 \(^2\) \( ^0 \)) \( ^2\Pi_\frac{1}{2} \) levels of NCS they observed.27 For Sears resonance, they introduced the \( F \) parameter27

\[
F = \frac{1}{\Delta E} \left( \frac{1}{2} AL_e \right) \left( \frac{1}{2} VL_e \right).
\]

He et al. suggested that there are two kinds of \( F \) for \( \Delta K = 0 \) and \( = \pm 2, \)28 while Northrup and Sears adopted that for only the \( \Delta K = 0 \) term in their analysis. In this work, two independent parameters, \( F_0 \) and \( F_2 \), for Sears resonance were adopted

\[
F_0 = 2 \times \frac{1}{\Delta E} \left( \frac{1}{2} AL_e \right) \left( \frac{1}{2} VL_e \right) \quad (\Delta K = 0),
\]

\[
F_2 = 2 \times \frac{1}{\Delta E} \left( \frac{1}{2} AL_e \right) \left( \frac{1}{2} VL_e \right) \quad (\Delta K = \pm 2),
\]

where the factor 2 in each of \( F_0 \) and \( F_2 \) corresponds to two equivalent terms at the right hand side of Eqs. (12) and (13) in Ref. 28. The constants on Sears resonance will be discussed in Subsection IV C below. The diagonal terms of the vibronic Hamiltonian at the present fifth stage are the same with those at the fourth step, i.e., Eq. (1), and the off-diagonal terms in the \( K \) blocks are also the same,

\[
H_{\text{ev}}^{5\text{th}} = H_{\text{ev}}^{4\text{th}} + H_{\text{Sears}},
\]

where \( H_{\text{Sears}} \) is the Hamiltonian for the Sears resonance. In the present fifth step, we need to construct the off-diagonal matrix blocks for \( \Delta K = \pm 1 \), which is schematically shown in Fig. 4 in Ref. 28. Using the two parameters, \( F_0 \) and \( F_2 \), and using the basis set of the 2D-HO, |\( P; \Lambda; v_2, l, v_3 \rangle = |\Lambda\rangle |\Sigma\rangle |K; v_2, l\rangle v_3 \rangle v_3 \rangle, \) the elements in the off-diagonal blocks for \( \Delta K = 0 \) and \( = \pm 1 \), respectively, are calculated as listed in Table I. Our elements were confirmed with those by He et al.,28 but with one exception; in their matrix elements, there is an additional factor of 2 only for the term with \( \Delta K = \pm 2 \), but not for \( \Delta K = 0 \). Because we use two independent parameters, \( F_0 \) and \( F_2 \), the additional factor 2 gives no effects on the present numerical analysis. The matrix elements for Sears resonance will be discussed with results from the present analysis in Subsection IV C below. Our code was checked using the GeCH and GeCD \( \tilde{X} \) \( ^2\Pi \) systems,28 where the Sears term is included in both, while the Fermi term is only included in the former.

Incorporating the code above into the parameter optimization routine, an analysis code has been established. The matrix to be solved is the size of 100 × 100, since \( v_3 \leq 4 \) has been taken. After the fifth step with Sears resonance, the \( P = -\frac{1}{2} \) block has only contribution of the \( K = 0 \) component, though the others have those from the two \( K \) components, \( K = P - \frac{1}{2} \) and \( =P + \frac{1}{2} \). The R-T parameter, \( \epsilon \), has been optimized as \( \epsilon \omega_2 \), because, in the present formulation, \( \epsilon \) always appeared as \( \epsilon \omega_2 \) (cf. Eqs. (6) and (7) below). The vibronic level energy is measured from the lowest level, (00 \(^0\)) \( ^2\Pi_\frac{1}{2} \), i.e., the energy of the level is taken as the standard and is set to be 0 cm\(^{-1}\). For the optimization, i.e., to calculate Jacobian matrix, numerical derivatives of the Hamiltonian by the parameters were adopted. Although Hellmann-Feynman theorem was tried, it was inefficient, which will be discussed in Subsection IV E below.

Using our computer code thus constructed, we could analyze the vibrational structure of the dispersed fluorescence spectra of the SiCN \( \tilde{X} \) \( ^2\Pi \) system with reasonable accuracy.
But the present analysis was not straightforward, because the good quantum number in the present analysis is only $P$, as mentioned above. Besides the $P$ quantum number, number of the order of its eigen value in each $P$ block can only characterize the observed vibronic levels. We practically took the following iterative procedure: (1) the levels perturbed lightly were initially analyzed using the computer code and assuming trial molecular constants. (2) Comparing the observed, but unassigned, level energies with the simulated eigen values, the numbers of the order were attributed to the unassigned levels. (3) Including the newly attributed levels, the trial constants were improved, and (4) procedure (1) was executed again using all of the levels attributed and adopting the constants improved. Procedures (1) ~ (4) have been iterated, until all of the observed bands had been analyzed. The results and molecular constants obtained by the iterative procedure of this routine are shown in Tables II and III, respectively, and all of the eigen values and the coefficients of the basis functions for the eigen state, i.e., the elements of the eigen vectors, are obtainable as in the supplementary material.

The eigen states below ~2500 cm$^{-1}$ in the $P = \pm \frac{1}{2}, + \frac{3}{2}$, and $+ \frac{5}{2}$ blocks are also shown in Figs. 6–8, respectively, with their basis functions and the level energies observed. The vibronic structure of the pure $v_2$ bending mode below ~1000 cm$^{-1}$ is shown in Fig. 9. Some of the eigen vectors, which are needed in the following discussions, and one of the components of which has >10%, are extracted in Table IV from the supplementary material.

The energies of the three vibrational levels, $\tilde{X}$ (01$^10$) $\mu$ 2Σ$^-(+)$, $2\Delta_1$, and $2\Delta_2$, as listed in Table II are consistent with those derived from our hot band analysis$^{11}$ within the experimental accuracies. (In Fig. 8 of our previous paper,$^{11}$ the level energy of $\tilde{X}$ (01$^00$) $\kappa$ 2Σ(+)) is mentioned, but this level has not been observed, and the energy is a value estimated under perturbation treatment.) The parity of the vibronic level is easily determined from the signs of the coefficients of its eigen vector. The parities of the (01$^10$) 2Σ levels are consistent with our previous study,$^{11}$ and as an example, this is shown below.

The 2nd and 4th eigen vectors in the $P = + \frac{1}{2}$ block have the $|\pm\rangle|\frac{1}{2}; 1, \mp 1\rangle|0\rangle$ bases as their major components. As listed in Table IV, the coefficients of the $|\pm\rangle|\frac{1}{2}; 1, +1\rangle|0\rangle$ and $|\pm\rangle|\frac{1}{2}; 1, -1\rangle|0\rangle$ bases are +0.8941 and -0.4104, and +0.3969 and +0.8148, for 2nd and 4th, respectively, in the present numerical analysis. The signs of the coefficients indicate that the lower and higher levels, 2nd and 4th, respectively, are attributed to $\tilde{X}$ (01$^00$) $\mu$ 2Σ(+)) and $\kappa$ 2Σ(+), respectively, because they have the opposite and same sign, respectively. On the basis of the intensity distribution of the rotational structure of the $\tilde{A}$ (01$^00$) 2Π$-\tilde{X}$ (01$^00$) $\mu$ 2Σ(+)) hot band, the parity of the lower level has been resulted to be (-) in our previous study,$^{11}$ which agrees with the present vibronic analysis. These parity assignments also agree with the sign of the R-T parameter, $\epsilon$; it is defined as $\epsilon = \frac{V^+ - V^-}{V^+ + V^-} = \frac{(\omega^+)^2 - (\omega^-)^2}{(\omega^+)^2 + (\omega^-)^2}$, where $V^+$ and $V^-$ are the harmonic potentials split by the R-T effect, and $\omega^+$ and $\omega^-$ are their bending frequencies, respectively, and then $+\text{ and } -$ sign of $\epsilon$ mean $V^+ > V^-$ and $V^+ < V^-$, respectively. The

<table>
<thead>
<tr>
<th>$\Lambda$</th>
<th>Transitions$^a$</th>
<th>Matrix elements$^b,c$</th>
<th>Notation in Fig. 4 in Ref. 28$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda = 0$</td>
<td>$A\Sigma = +1$</td>
<td>$A\Delta = +1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
<tr>
<td>$\Lambda = -1$</td>
<td>$A\Sigma = +1$</td>
<td>$A\Delta = +1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
<tr>
<td>$\Lambda = -1$</td>
<td>$A\Delta = +2$</td>
<td>$A\Delta = +1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
<tr>
<td>$\Lambda = +2$</td>
<td>$A\Delta = +1$</td>
<td>$A\Delta = +1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
<tr>
<td>$\Lambda = +2$</td>
<td>$A\Delta = -1$</td>
<td>$A\Delta = -1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
<tr>
<td>$\Lambda = +2$</td>
<td>$A\Delta = -1$</td>
<td>$A\Delta = -1$</td>
<td>$F_0 \sqrt{\frac{\nu_1 + \nu_2}{2}}$</td>
</tr>
</tbody>
</table>

$^a$Transition means $(P; K; \Delta\Lambda; \Lambda; \Delta\Sigma; \Sigma; \nu_1; \nu_2; \nu_3; P, K; \Delta\Lambda; \Lambda; \Delta\Sigma; \Sigma; \nu_1; \nu_2, l^\prime)$, where $l^\prime = (K + \Delta\Lambda) - (\Lambda + \Delta\Lambda)$ and $l'' = K - \Lambda$.

$^b$For convenience for the readers, the elements for $A\Delta = \pm 1$ are shown, though those for $A\Delta = 0$ are only in Ref. 28.

$^c$The $F_2$ is 2×$F_0$ in Ref. 28 under a limited situation with a single $2\Pi - 2\Sigma$ coupling. See more details on the additional factor 2 for the $F_2$ elements in the text, Subsection IV C.

$^d$By definition, $\langle P; K; \Delta\Lambda; \Lambda; \Delta\Sigma; \Sigma; \nu_1; \nu_2; \nu_3; P, K; \Delta\Lambda; \Lambda; \Delta\Sigma; \Sigma; \nu_1; \nu_2, l^\prime\rangle$, where $l^\prime = K - \Lambda$ and $l'' = (K + \Delta\Lambda) - (\Lambda + \Delta\Lambda)$.

This element is equivalent to Eq. (13) in Ref. 27.
TABLE II. Vibrational levels of the $^3\Pi$ state (cm$^{-1}$).

<table>
<thead>
<tr>
<th>$P$</th>
<th>Level$^b$</th>
<th>Obs.</th>
<th>Obs.-calc.</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>+0.5</td>
<td>(00)$^2\Pi_{\frac{1}{2}}$</td>
<td>2282.0</td>
<td>−0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>+0.5</td>
<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>2586.3</td>
<td>−0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>+1.5</td>
<td>(00)$^2\Pi_{\frac{1}{2}}$</td>
<td>2672.4</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>+1.5</td>
<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>1952.1</td>
<td>0.1</td>
<td>1.0</td>
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<tr>
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<td>(00)$^2\Pi_{\frac{1}{2}}$</td>
<td>1941.8</td>
<td>−1.1</td>
<td>1.0</td>
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<tr>
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<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>1839.1</td>
<td>−2.3</td>
<td>1.0</td>
</tr>
<tr>
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<td>1715.6</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
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<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>2001.3</td>
<td>−2.7</td>
<td>1.0</td>
</tr>
<tr>
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<td>1982.3</td>
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<td>1912.8</td>
<td>1.4</td>
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<tr>
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<tr>
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<tr>
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<td>993.9</td>
<td>−1.9</td>
<td>1.0</td>
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<tr>
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<tr>
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<td>1971.3</td>
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<td>2061.8</td>
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<td>1607.5</td>
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<td>1873.2</td>
<td>1.7</td>
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<td>801.5</td>
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<td>(00)$^2\Pi_{\frac{1}{2}}$</td>
<td>783.1</td>
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<td>1.0</td>
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<td>+1.5</td>
<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>602.3</td>
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<td>689.4</td>
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<td>(00)$^2\Pi_{\frac{3}{2}}$</td>
<td>658.1</td>
<td>0.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$Order of the eigen value in each $P$ block.
$^b$The assignments are tentative. See text.

As mentioned at the end of Subsection III A, the vibrational structure analyzed by the perturbation approach had not only had a regular structure, but also contained a chaotic one. Even at present after the success of the numerical analysis, the levels belonging to the regular structure are a few, and some of the vibrational levels have chaotic characteristics in view of the 2D-HO used as the basis set in the present numerical analysis. Because of this, we have not been able to give precise vibronic assignments for some of the levels analyzed, but just vibronically labeled, referring the largest component of their eigenvectors; in other words, the vibronic assignments for some of the levels are thus meaningless. Two examples of this situation are shown below (to emphasize this situation, we do not use the word “assignment,” but prefer to attribution of the $(−)$ parity to the lower R-T pair thus agrees with the $+$ sign of $\epsilon$ determined.

TABLE III. Molecular constants (cm$^{-1}$ except $\epsilon$).

<table>
<thead>
<tr>
<th></th>
<th>This work$^a$</th>
<th>Reference 11</th>
<th>Reference 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_2$</td>
<td>246.74(82)</td>
<td>236$^b$</td>
<td></td>
</tr>
<tr>
<td>$\epsilon\omega_2$</td>
<td>83.72(90)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.339 30$^c$</td>
<td>0.38$^d$</td>
<td>0.3043$^e$</td>
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<tr>
<td>$\omega_3$</td>
<td>584.3(11)</td>
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<td>$\omega_2$</td>
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<td>$\omega_3$</td>
<td>144.2(17)</td>
<td>146.2258$^f$</td>
<td>141$^f$</td>
</tr>
<tr>
<td>$g_4$</td>
<td>−0.136(57)</td>
<td></td>
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</tr>
<tr>
<td>$g_4$</td>
<td>−0.134(60)</td>
<td></td>
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<tr>
<td>$g_\kappa$</td>
<td>−0.18(59)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W_1$</td>
<td>14.046(99)</td>
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</tr>
<tr>
<td>$W_2$</td>
<td>4.3(11)</td>
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<tr>
<td>$x_{33}$</td>
<td>−5.47(30)</td>
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</tr>
<tr>
<td>$x_{23}$</td>
<td>3.37(21)</td>
<td></td>
<td></td>
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<tr>
<td>$\alpha_3$</td>
<td>9.9(14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_0$</td>
<td>4.85(98)</td>
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<tr>
<td>$F_2$</td>
<td>7.8(21)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>1.75(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Numbers in parentheses are one standard deviation in units of the last significant digit.
$^b$Estimated value.
$^c$Derived from the $\omega_2$ and $\epsilon\omega_2$ constants above.
$^d$0.32 and 0.30 for Refs. 7 and 9, respectively.
$^e$Derived from the $A_{el}$ constants in the $(00)^0\Pi^0\Pi$ and $(01)^0\Delta^2\Sigma$ levels.
$^f$SO splitting at the $(00)^0\Pi^0\Pi$ level.
$^g$One standard deviation for the fitting analysis.
The energy diagram, below ~2500 cm\(^{-1}\), of the basis functions used for the present numerical analysis and of the eigen states derived from the analysis of the \(P = +\frac{1}{2}\) block. The \(v_3 = 4\) stack is included in the analysis, but is omitted here. The functions denoted by solid lines exist, but those denoted by broken lines do not. The basis functions are doubly degenerate with \(\pm K\) except ones of the unique levels, which is the lowest level in each \(v_3\) stack except the \(\Sigma\) vibronic level (\(K = 0\)). Although the functions are also degenerate with \(\pm |K\rangle\), the \(+|K\rangle\) component has been taken in the analysis (see more details in the text, Sec. III B). The energies of the basis functions are the harmonic vibrational terms in Eq. (1), \(E_{\nu K} = \omega_1 (v_1 + 1) + \omega_2 (v_2 + 1) + \omega_3 v_3 + \Delta \Sigma\), but they are measured from the lowest level, (0000) \(^3\Pi_2\), as the same with those of the eigen states calculated. The observed levels with large deviation are expressed by dotted lines.

<table>
<thead>
<tr>
<th>(\Sigma)</th>
<th>(K = 0) ((\Sigma))</th>
<th>(K = 1) ((\Pi))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+\frac{1}{2})</td>
<td>calc. obs.</td>
<td></td>
</tr>
<tr>
<td>(-\frac{1}{2})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 6.** The energy diagram, below ~2500 cm\(^{-1}\), of the basis functions used for the present numerical analysis and of the eigen states derived from the analysis of the \(P = +\frac{1}{2}\) block. The \(v_3 = 4\) stack is included in the analysis, but is omitted here. The functions denoted by solid lines exist, but those denoted by broken lines do not. The basis functions are doubly degenerate with \(\pm K\) except ones of the unique levels, which is the lowest level in each \(v_3\) stack except the \(\Sigma\) vibronic level (\(K = 0\)). Although the functions are also degenerate with \(\pm |K\rangle\), the \(+|K\rangle\) component has been taken in the analysis (see more details in the text, Sec. III B). The energies of the basis functions are the harmonic vibrational terms in Eq. (1), \(E_{\nu K} = \omega_1 (v_1 + 1) + \omega_2 (v_2 + 1) + \omega_3 v_3 + \Delta \Sigma\), but they are measured from the lowest level, (0000) \(^3\Pi_2\), as the same with those of the eigen states calculated. The observed levels with large deviation are expressed by dotted lines, and the level with the largest deviation is marked by *.

<table>
<thead>
<tr>
<th>(\Sigma)</th>
<th>(K = 0) ((\Sigma))</th>
<th>(K = 1) ((\Pi))</th>
<th>(K = 2) ((\Delta))</th>
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<td>(+\frac{1}{2})</td>
<td>calc. obs.</td>
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<tr>
<td>(-\frac{1}{2})</td>
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</tbody>
</table>

**FIG. 7.** The energy diagram, below ~2500 cm\(^{-1}\), of the basis functions used for the present numerical analysis and of the eigen states derived from the analysis of the \(P = +\frac{1}{2}\) block. The \(v_3 = 4\) stack is included in the analysis, but is omitted here. The functions denoted by solid lines exist, but those denoted by broken lines do not. The basis functions are doubly degenerate with \(\pm K\) except ones of the unique levels, which is the lowest level in each \(v_3\) stack except the \(\Sigma\) vibronic level (\(K = 0\)). Although the functions are also degenerate with \(\pm |K\rangle\), the \(+|K\rangle\) component has been taken in the analysis (see more details in the text, Sec. III B). The energies of the basis functions are the harmonic vibrational terms in Eq. (1), \(E_{\nu K} = \omega_1 (v_1 + 1) + \omega_2 v_2 + \Delta \Sigma\), but they are measured from the lowest level, (0000) \(^3\Pi_2\), as the same with those of the eigen states calculated. The observed levels with large deviation are expressed by dotted lines, and the level with the largest deviation is marked by *.

use “label” as the meaning of just “label,” but not “assign,” throughout this paper:

1. The first example is the (07\(^1\)\(^0\)) \(\kappa \Sigma^{(\pm)}\) level. This level observed at 1873.2 cm\(^{-1}\) corresponds to the 34th eigen state in the \(P = +\frac{1}{2}\) block obtained by the present numerical analysis. The coefficients of the major components of the 34th eigen vector are listed in Table IV, and the coefficients show this level has a contribution from the (07\(^0\)\(^0\)), (05\(^1\)\(^1\)), and (07\(^1\)\(^1\)) levels. Square-sums of them are 0.2849, 0.1744, and 0.1104, respectively, and the level is thus “labeled” as (07\(^0\)\(^0\)) \(\kappa \Sigma^{(\pm)}\), where \(\kappa\) (or (+)) is recognized from the same sign of the coefficients of the two (07\(^0\)\(^0\)) bases. Note that this 1873.2 cm\(^{-1}\) level is “labeled” (07\(^0\)\(^0\)) \(\kappa \Sigma^{(\pm)}\), but also has considerable contributions from (07\(^1\)\(^1\)) and (05\(^1\)\(^1\)).

2. The second is (09\(^0\)\(^0\)) \(\mu \Delta^{(\pm)}\), and this level observed at 1971.3 cm\(^{-1}\) corresponds to the 34th eigen state in the \(P = +\frac{1}{2}\) block obtained by the present numerical analysis, the major components of which are also listed in Table IV. Square-sums of the coefficients of the basis functions are 0.3105, 0.1630, and 0.1932, for the vibronic levels, (09\(^0\)\(^0\)), (05\(^1\)\(^1\)), and (07\(^1\)\(^1\)), respectively, and the level is thus “labeled” as (09\(^0\)\(^0\)) \(\mu \Delta^{(\pm)}\), where \(\mu\) is recognized from the different sign of the coefficients of the two (09\(^0\)\(^0\)) bases. Note that this 1971.3 cm\(^{-1}\) level is “labeled” (09\(^0\)\(^0\)) \(\mu \Delta^{(\pm)}\), but also has considerable contributions of (05\(^1\)\(^1\)) and (07\(^1\)\(^1\)).

The constants obtained are all consistent with those reported. Although some of them, \(gK\), \(\epsilon_3\), and \(F_2\), are almost within their errors, they are needed to achieve the present reasonable analysis (which means most of them may not be ignored). Some of them, \(\epsilon_2\), \(\epsilon_\omega\), \(\epsilon (\epsilon_\omega)\), and \(A\), agree with those estimated by the R-T formulation derived for low-lying and restricted levels using perturbation treatment.\(^{11,12}\) Under the third order correction, the \(A\) constant at \(K\) levels, \(A_{\text{eff}}\), is expressed as\(^{14}\)

\[
A_{\text{eff}} = A \left(1 - \frac{1}{8} \epsilon^2 K (K + 1)^2 \right).
\]

Using the \(\epsilon\) constants obtained, and adopting \(A_{\text{eff}}\) at the vibrationless level, 140.82 cm\(^{-1}\), \(A\) is calculated to be 145 cm\(^{-1}\), and this agrees with that obtained in the present analysis. The two parameters, \(W_1\) and \(W_2\), for Fermi resonance
are related to the parameters for the two bending potentials, symmetric and asymmetric ones, respectively, split by the R-T interaction. The tendency of the Fermi resonance constants, \( W_1 > W_2 \), is consistent with those reported for the other \( 2 \Pi \) electronic states, such as CO\(_2\), NCS, and NCO. Although the criterion of Fermi resonance is well-known as 
\[
\omega_1 \approx 2 \omega_2
\]
where \( \omega_1 \) and \( \omega_2 \) are stretching and bending vibrational modes, respectively, even in the condition, \( \omega_3 = 2 \omega_2 = 584 - 493 = 91 \text{ cm}^{-1} \), Fermi resonance is considerable in the present SiCN system. It is thought to be not surprising because of the chaotic appearance of the vibronic levels of the SiCN \( 2 \Pi \) state and relation, \( g_4 \equiv \tilde{g}_4 \). \( g_K \) is also negative, but it is within its error range including 0 showing a possibility of negligible \( g_K \) constant. This is interpreted as weak H-T interaction in the present system. It must be noticed that, although the “pure” H-T interaction seems to be negligible, the second-order interaction combined with H-T and SO, i.e., Sears resonance, must be considerable. The strength of the H-T interaction will be discussed with the Sears constants in Subsection IV C below. The anharmonic constants with the \( v_3 \) mode, \( x_{33} \) and \( x_{23} \), and the \( v_3 \) mode dependence of \( A \), \( \alpha_3 \), also follow the general trend accepted widely.

C. The vibronic levels of the \( \tilde{X} \ 2 \Pi \) state

When considerable Fermi and Sears couplings, as well as R-T, occur in bending vibrational structure, like the present SiCN system, it is not easy to characterize the vibronic levels, because of less quantum numbers to characterize the levels and of the chaotic appearance, i.e., widely and complex mixings among the levels. Even in such systems, coefficients of the eigen functions can characterize the levels, as already mentioned in Subsection III B that the coefficients have utilized how to label the observed levels. In this subsection, for the present numerical analysis and of the eigen states derived from the analysis of the \( P = \frac{1}{2} \) block. The \( v_3 = 4 \) stack is included in the analysis, but is omitted here. The functions denoted by solid lines exist, but those denoted by broken lines do not. The basis functions are doubly degenerate with \( \pm \) except ones of the unique levels, which is the lowest level in each \( v_3 \) stack except the \( \Sigma \) vibronic level (\( K = 0 \)). Although the functions are also degenerate with \( \pm [K] \), the degeneracy does not get resolved in the present analysis, and the \( \pm [K] \) component has been taken in the analysis (see more details in the text, Sec. III B). The energies of the basis functions are the harmonic vibrational terms in Eq. (1), \( E_{00} = \omega_2 (v_2 + 1) + \omega_3 v_3 + A \Sigma \), but they are measured from the lowest level, \( (0000)^2 \Pi_1/2 \), as the same with those of the eigen states calculated.
TABLE IV. Vibrational levels and the coefficients of their own eigenvectors (an extract list from the full version provided as a supplementary material).

<table>
<thead>
<tr>
<th>Level</th>
<th>Energy</th>
<th>Vector</th>
<th>Coefficients of vectors^a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(−)</td>
</tr>
<tr>
<td>(01(^2)0) ( \kappa ) ( ^2\Sigma^+ )</td>
<td>2017</td>
<td>(2nd)</td>
<td>+0.8941</td>
</tr>
<tr>
<td>(01(^4)0) ( \kappa ) ( ^2\Pi)</td>
<td>421.8</td>
<td>(4th)</td>
<td>+0.3969</td>
</tr>
<tr>
<td>(02(^2)0) ( \mu ) ( ^2\Pi)</td>
<td>398.9</td>
<td>(3rd)</td>
<td>+0.1434</td>
</tr>
<tr>
<td>(02(^0)0) ( \kappa ) ( ^2\Pi)</td>
<td>689.4</td>
<td>(7th)</td>
<td>−0.0345</td>
</tr>
<tr>
<td>(07(^4)0) ( \kappa ) ( ^2\Sigma^+ )</td>
<td>1873.2</td>
<td>(34th)</td>
<td>−0.0137</td>
</tr>
<tr>
<td>(09(^4)0) ( \mu ) ( ^2\Delta)</td>
<td>1971.3</td>
<td>(34th)</td>
<td>−0.3495</td>
</tr>
<tr>
<td>(02(^2)0) ( \mu ) ( ^2\Pi)</td>
<td>1574.1</td>
<td>(24th)</td>
<td>+0.3325</td>
</tr>
<tr>
<td>(02(^0)2) ( \mu ) ( ^2\Pi)</td>
<td>1581.8</td>
<td>(25th)</td>
<td>−0.3069</td>
</tr>
<tr>
<td>(02(^0)1) ( \mu ) ( ^2\Pi)</td>
<td>993.9</td>
<td>(12th)</td>
<td>−0.1661</td>
</tr>
<tr>
<td>(00(^2)2) ( \mu ) ( ^2\Pi)</td>
<td>1145.1</td>
<td>(14th)</td>
<td>+0.1852</td>
</tr>
<tr>
<td>(00(^2)2) ( \mu ) ( ^2\Pi)</td>
<td>1155.7</td>
<td>(15th)</td>
<td>−0.0462</td>
</tr>
<tr>
<td>(02(^0)1) ( \kappa ) ( ^2\Pi)</td>
<td>1304.0</td>
<td>(18th)</td>
<td>−0.6186</td>
</tr>
<tr>
<td>(06(^0)0) ( \mu ) ( ^2\Pi)</td>
<td>1607.5</td>
<td>(26th)</td>
<td>−0.0173</td>
</tr>
<tr>
<td>(06(^0)0) ( \mu ) ( ^2\Pi)</td>
<td>2072.6</td>
<td>(40th)</td>
<td>+0.2025</td>
</tr>
<tr>
<td>(06(^2)0) ( \mu ) ( ^2\Pi)</td>
<td>1839.1</td>
<td>(30th)</td>
<td>+0.1043</td>
</tr>
<tr>
<td>(02(^2)0) ( \kappa ) ( ^2\Pi)</td>
<td>1912.8</td>
<td>(32nd)</td>
<td>+0.2099</td>
</tr>
<tr>
<td>(01(^1)2) ( \mu ) ( ^2\Sigma^− )</td>
<td>1373.4</td>
<td>(20th)</td>
<td>+0.0226</td>
</tr>
<tr>
<td>(14(^1)1) ( \kappa ) ( ^2\Pi)</td>
<td>2229.1</td>
<td>(22nd)</td>
<td>+0.2595</td>
</tr>
<tr>
<td>(15(^1)7) ( \kappa ) ( ^2\Pi)</td>
<td>2369.9</td>
<td>(23rd)</td>
<td>+0.2369</td>
</tr>
<tr>
<td>(16(^1)3) ( \kappa ) ( ^2\Pi)</td>
<td>2763.3</td>
<td>(27th)</td>
<td>+0.1909</td>
</tr>
</tbody>
</table>
\begin{table}
\centering
\begin{tabular}{llllllll}
\hline
Level & Energy & Vector & $|+\rangle_{1/2:0,0,1}$ & $|+\rangle_{1/2:2,0,0}$ & $|+\rangle_{1/2:2,0,0}$ & Coefficients of vectors$^a$
\hline
$(00^1l)^2\Pi_1$ & 576.0 & 5th & -0.9534 & +0.2232 & \textbf{-0.0182} &
\hline
$(01^1l)^2\Sigma^+(-)$ & (596)$^d$ & 6th & +0.7406 & -0.4879 & +0.1900 & -0.1762 & -0.1343 & +0.0565 &
\hline
$(01^1l)^2\Sigma^+$ & 789.5 & 9th & +0.1029 & -0.1532 & +0.0575 & -0.0378 & +0.8690 & -0.4022 &
\hline
$(05^1l)^2\Sigma^+(*)$ & 974.5 & 11th & +0.5334 & +0.5431 & -0.3362 & +0.1495 & -0.1367 & -0.4220 &
\hline
$(01^1l)^2\Sigma^+(-)$ & 1018.6 & 13th & +0.0838 & -0.3704 & -0.5381 & +0.4242 & +0.1098 & +0.3311 &
\hline
$(134l)^d$ & 19th & +0.0265 & -0.0390 & -0.5158 & +0.0437 & -0.0022 & -0.0027 &
\hline
$(03^1l)^2\Delta_1$ & 1205.9 & 14th & -0.1102 & -0.3962 & +0.0863 & +0.1293 & -0.0549 & -0.3111 & +0.6444 &
\hline
$(00^2l)^2\Pi_1$ & 1260.5 & 15th & -0.2201 & -0.3970 & -0.2981 & -0.2422 & +0.6974 & +0.0616 & -0.1340 &
\hline
$(00^2l)^2\Pi_1$ & 1313.4 & 16th & +0.1297 & +0.2442 & +0.3233 & +0.4564 & +0.6486 & -0.0305 & +0.0635 &
\hline
$(01^2l)^2\Delta_1$ & (138l)$^d$ & 18th & -0.2128 & -0.1668 & +0.4420 & -0.0284 & -0.8201 &
\hline
$(142l)^d$ & 20th & +0.6268 & +0.3823 & -0.3126 & -0.1874 & -0.4319 &
\hline
$(158l)^d$ & 22nd & -0.3445 & -0.2189 & -0.5525 & -0.2779 & -0.1485 &
\hline
\end{tabular}
\end{table}

$^a$\langle P|\Lambda\rangle |v_l\rangle |v_o\rangle$, where $\Lambda$ shows its sign only. $P$s are all positive in the present numerical analysis, because positive $K$ is only considered (see Subsection III B).

$^b$\langle \Lambda\Sigma|K\rangle |v_l\rangle |v_o\rangle$, where $\Lambda$ shows its sign only. $K$s are all positive in the present numerical analysis (see Subsection III B).

$^c$Less than 10%.

$^d$The energy in parenthesis is that calculated, and the level has not been observed yet.
we considered some characteristic vibronic levels resulted in the
present analysis, using the coefficients and referring
the information provided from the computational work,10 because
the work gives surprisingly good predictions for the vibronic
level structure.

1. Identically labeled vibronic levels

As shown in Table II, we need to identically label two
observed levels, (00') 2Π1, (00') 2Π1, and (02') 2Π1. The first and second (00')
levels will be discussed in Subsections III C 2 and III C 3,
respectively, because each of them is also one of the typical
examples of levels spread widely or of those with relatively
large deviation, respectively, and the third is only mentioned
in this subsection.

a. (02') 2Π1. As shown in Table II, we need to attribu-
te two observed levels, 1574.1 and 1581.8 cm\(^{-1}\), to
(02') 2Π1. There is no information from computational
sides for this level (such as REF\(^\text{10}\)). The two observed levels
correspond to the 24th and 25th eigen states in the \(P = + \frac{1}{2}\)
block in the present numerical analysis. Coefficients of the
major 2D-HO basis functions consisting of their eigen vectors
are shown in Table IV. The coefficients indicate that the
eigen states have contribution from the bases, |±\((\frac{1}{2}, 5, \pm 1)\rangle|1\rangle, |
±\((\frac{1}{2}, 1, 1, 1)\rangle|2\rangle\rangle, and |−/+\rangle\rangle|\(\frac{3}{2}, 2, +2, 0\rangle|2\rangle\rangle, which
 correspond to three vibronic levels, (05')\(1\), (01')\(2\), \(2\)\(Σ\), and (02') 2Π1,
respectively, under the pure 2D-HO system, i.e., 2D-HO
without any perturbation. The last component has the largest
contribution, and the coefficients of the two \(\Lambda = +1\) and
−1 components, −0.2036 and +0.5437, and −0.2671 and
+0.5358, for the 24th and 25th states, respectively, are
 almost the same including their sign, and both states are thus
identically labeled to (02') 2Π1. The second contribution,
|±\((\frac{1}{2}, 1, 1)\rangle|2\rangle\rangle, is its \(κ\) component because of the same sign
of the two coefficients for the two \(\Lambda = ±1\) components, and
the coefficients of the second and last contributions,
|±\((\frac{1}{2}, 1, 1)\rangle|2\rangle\rangle and |−/+\rangle\rangle|\(\frac{3}{2}, 2, +2, 0\rangle|2\rangle\rangle, indicate that the
24th and 25th states have Sears resonance between them, the
(01')\(2\) \(2\)\(Σ\) and (02') 2Π1 levels, respectively.
This Sears resonance is a \(v_2 + v_3\) combination level version of the
resonance typical in the SiCN X 2Π1 system which occurs in the
pure \(v_2\) levels, and which will be discussed in Subsection IV B.
The \(2\)\(Σ\) components have following two characteristics: (1) The \(2\)\(Σ\)
coefficients of the 24th and 25th eigen states are almost the
same (though that of the \(\Lambda = +1\) component has about 3 times
larger than that of \(\Lambda = −1\) in each state), but have a different
sign (though the two \(\Lambda\) components have the same sign in each
state), and these indicate the \(2\)\(Σ\) contributions to the two states
are almost the same, and (2) the \(κ\) \(2\)\(Σ\) level has not been
observed yet, while (01')\(2\) \(2\)\(Σ\) has been observed as listed
in Table II, and this indicates that the \(κ\) level is absorbed in the
identically labeled (02') 2Π1 levels. The first contribution,
|±\((\frac{1}{2}, 5, \pm 1)\rangle|1\rangle\rangle, is its \(μ\) component because of different sign
of the two coefficients for their two \(\Lambda = ±1\) components.
The coefficients of (07')\(0\) \(2\)\(Σ\), as listed in Table IV and
as considered in Subsection III B, suggest Fermi resonance
between the (05')\(1\) and (07')\(0\) levels, and this indicates the
24th and 25th states have contribution to levels spread widely
with span, ~300 cm\(^{-1}\) (cf. the (07')\(0\) level is at 1873 cm\(^{-1}\),
while the present (02')\(2\) levels are at 1581 and 1574 cm\(^{-1}\)).
It is thus concluded that the contributions from the first
and second components mentioned above induce heavy mixing
among the levels and result in the duplication of (02')\(2\) \(2\)Π1.
Sears resonance mentioned above in this paragraph will be
discussed in Subsection IV B using more typical examples.

2. Vibronic levels spread widely

da. (00') 2Π1. As shown in Table II, we need to attribute
two observed levels, 1145.1 and 1155.7 cm\(^{-1}\), to the (00') 2Π1
unique level. In contrast, the computational study attributed
only the former, 1147 cm\(^{-1}\), to the level.\(^\text{10}\) Our two levels
correspond to the 14th and 15th eigen states in the \(P = + \frac{1}{2}\)
block in the present numerical analysis. Coefficients of the
major 2D-HO basis functions consisting of their eigen vectors
are shown in Table IV. The two states share almost evenly
the basis function, |+\rangle\rangle|\(\frac{3}{2}, 0, 0\rangle|2\rangle\rangle, as their eigen vectors with
the coefficients +0.6470 and −0.6059 for 14th and 15th,
respectively, and then it is difficult to assign uniquely and
definitely, and both are thus identically labeled to (00') 2Π1.
The basis function, |+\rangle\rangle|\(\frac{3}{2}, 0, 0\rangle|2\rangle\rangle, is also spread into the
16th eigen state with its coefficient +0.3698. The 14th eigen state
also contains |+\rangle\rangle|\(\frac{3}{2}, 4, 0\rangle|0\rangle\rangle and |−\rangle\rangle|\(\frac{3}{2}, -2, +2\rangle|1\rangle\rangle,
with the coefficients, +0.3893 and −0.3813, respectively,
which indicate the existence of Fermi resonance among the
(04')\(0\), (02')\(1\), and (00')\(2\) levels. One of the basis functions,
|−\rangle\rangle|\(\frac{3}{2}, -2, +2\rangle|1\rangle\rangle, is also considerable in the 12th, 16th, and
18th eigen states with coefficients of −0.3907, +0.3438,
and −0.6472, respectively, and its positive \(Λ\) component,
|+\rangle\rangle|\(\frac{3}{2}, 2, 0\rangle|1\rangle\rangle, is considerable in 12th and 18th with those
of +0.7910 and −0.4252. The 12th and 18th bases give the
major component of R-T pair for (02')\(1\) 2Π1. This, and the
previous (02')\(2\) \(2\)Π1 also, is one of the typical examples of
the widely spread basis function by Fermi resonance (within
the same \(K\) ) and R-T interaction with a span over 300 cm\(^{-1}\).
Similar mixing is recognized at several places, and the other
three examples are shown here.

b. (08')\(0\) \(μ\) and \(κ\) 2Π1. Both 1607.5 and 2072.6 cm\(^{-1}\)
levels observed are attributed to the 26th and 40th eigen
states in the \(P = + \frac{1}{2}\) block. As shown in Table IV, the
two, 26th and 40th, have a contribution of |−\rangle\rangle|\(\frac{3}{2}, 8, +2\rangle|0\rangle\rangle
and |+\rangle\rangle|\(\frac{3}{2}, 8, 0\rangle|0\rangle\rangle with −0.3186 and +0.5094, and −0.4392
and −0.3660, respectively, and this indicates that they are
the R-T pair for the (08')\(0\) 2Π1 vibronic level as listed
in Table II. The two also have a contribution of |+\rangle\rangle|\(\frac{3}{2}, 6, 0\rangle|0\rangle\rangle
and |−\rangle\rangle|\(\frac{3}{2}, 6, 0\rangle|1\rangle\rangle with −0.5153 and −0.1238, and +0.1381
and +0.3703, respectively, though one of each basis functions
has less than 10% contribution. This example indicates that
R-T is the most effective for the wide spread of vibronic
levels, and this also resulted from the largest coupling, \(εω_2\),
among those considered in the present analysis.

c. (00')\(3\) 2Π3. The levels at 1839.1 and 1912.8 cm\(^{-1}\)
are attributed to the 30th and 32nd states, respectively, in
the \(P = + \frac{1}{2}\) block, both of which have a contribution of
As listed in Table IV, the 22nd eigen vectors correspond to the latter is that both also have |
which are listed in Table II and will be considered in the present analysis, because the deviations are over 5 cm⁻¹, though they, except the last, are barely within our resolution.

\( \langle +|\frac{3}{2};2,2/0|\rangle \) with |−0.6908 and +0.3203, respectively, as

listed in Table IV. The former 30th is then labeled to (00\(^3\) \( \Sigma^+ \)), and this second orthonormal of the \( \nu_2 \) stretching level splits into over 70 cm⁻¹. It is considered that Fermi and R-T interactions induce this wide splitting: the reason for the former interaction is that both have considerable contribution of the four bases, |−/+\rangle\[3/2,2,2/0|\rangle (2) and |−/+\rangle\[3/2,4,2/0|\rangle (1) in addition to +|\frac{3}{2};0,0|\rangle (3), and that for the latter is that both also have |−/+\rangle\[3/2,4,2/0|\rangle (2) but with different phase in the two \( \pm \Lambda \) components for 30th and 32nd, though the other Fermi components have the same phase. The 32nd has |−/+\rangle\[3/2,2,2/0|\rangle (2) as the largest component, (+0.3496)\( + (+0.3714) = 0.2602\), and this is thus labeled to (02\(^2\) \( \kappa \Sigma^+ \)), though the others also give considerable contributions, 0.2041 and 0.2035, for |−/+\rangle\[3/2,4,2/0|\rangle (1) and |−/+\rangle\[3/2,4,2/0|\rangle (2), respectively.

d. (05\(^0\) \( \kappa \Sigma^+ \)). Although the \( \mu \) component has been observed as listed in Table II and will be considered in Subsection III C 3, this \( \kappa \) level has not been observed yet. As listed in Table IV, the 22nd eigen vectors correspond to the \( \kappa \) level, because this has relatively large coefficients of |±\rangle\[3/2,5;\pm 1|\rangle (0) and the coefficients have the same sign. The 23rd one also constitutes the \( \kappa \) level, though this has |±\rangle\[3/2,1;\mp 1|\rangle (2) as the largest coefficient. There is Fermi resonance in each of the two, i.e., among |±\rangle\[3/2,5;\mp 1|\rangle (0), |±\rangle\[3/2,3;\pm 1|\rangle (1), and |±\rangle\[3/2,1;\mp 1|\rangle (2). The difference in the 22nd and 23rd is only the sign of the last components, i.e., they correspond to \( \mu \) and \( \kappa \), respectively, for the last component, while both are \( \kappa \) for the other two components except the last (Table II). The \( \mu \) level of the last component is already labeled to the level at 1373.4 cm⁻¹, (01\(^2\) \( \mu \Sigma^+ \)). The 27th eigen state has considerable contribution of |±\rangle\[3/2,1;\mp 1|\rangle (2) with same phase, i.e., (01\(^2\) \( \kappa \Sigma^+ \)), and the 23rd and 27th are almost 1:1 mixing for the basis. It is thus considered that the levels are widely spread due to Fermi resonance among the (05\(^0\)), (03\(^1\)), and (01\(^2\)) levels.

Most of all levels observed are those consisting of some of the basis functions, and some of the vibrational labels (assignments, usually) given are thus diluted heavily and vibrational quantum numbers labeled (assigned, usually) are almost meaningless. Regarding the 2D-HO basis functions, this means a sort of chaotic characteristics of the vibrational levels for the \( \tilde{X} \) \( \tilde{2} \Pi \) state of SICN, even in those lying at ~1000 cm⁻¹. It is realized from Table IV that the major reason for the wide splitting of the vibronic levels is R-T. In the four examples above, Fermi resonance, as well as R-T, makes the vibronic labels invalid. Besides Fermi resonance, Sears resonance also induces the chaotic appearance, as already discussed in Subsection III C 1.

### 3. Vibronic levels with large deviation

As shown in Table II, most of all vibronic levels observed are fitted within deviations, <3 cm⁻¹, which is much better than our experimental accuracy, ±5 cm⁻¹. In the present analysis, there are four levels, (00\(^1\) \( \tilde{2} \Pi \)). As shown in Table II, both of the two levels at 1260.5 and 1313.4 cm⁻¹, corresponding to the 15th and 16th eigen states, respectively, in the \( P = + \frac{3}{2} \) block obtained by the present numerical analysis, are attributed to the (00\(^2\) \( \tilde{2} \Pi \)) unique level, and only the latter shows good agreement with that computed, 1312 cm⁻¹. The two 15th and 16th levels have the basis, |+\rangle\[3/2,0,0|\rangle (2), as their largest contributions, and they share it with almost 50\%:50\%; their coefficients are +0.6974 and +0.6486, respectively, as shown in Table IV. Accordingly, both are identically labeled to (00\(^2\) \( \tilde{2} \Pi \)).
IV. DISCUSSION

A. Sears resonance

As mentioned in Subsection III B, Sears resonance is a vibronic interaction between two vibrational levels on an electronic state, and the vibronic interaction is a second-order interaction combined with the H-T and SO interactions through the other electronic states. Accordingly, Sears resonance is automatically treated, when several electronic states coupled by R-T and SO are simultaneously treated, and computational works, such as the one by Brites et al.,10 typical of such treatment. In contrast, on considerations of spectra focused on an electronic state, such as vibrational analysis of experimentally obtained spectra like the present work, it is needed to include the second-order interaction through the other electronic state as a second-order perturbation, and Van Vleck transformation (it is also called as contract transformation or second-order perturbation) is known as one of the procedures to perform this treatment.31-33 The $g_K$ term is in a similar situation with Sears resonance. The $g_K$ term is introduced by Brown,25 and the term of a $\Sigma$ state is generated by the second-order interaction of the H-T coupling through $\Sigma$ and/or $\Delta$ states, and was derived using Van Vleck transformation. In contrast, even in the works on considerations of spectra focused on an electronic state, taking specific electronic states as the perturbers and adopting numerical diagonalization analysis including all of the states taken into account, we do not need to consider the $g_K$ term, and this procedure was actually performed by Guyacaq and Juneng.13 As mentioned in Subsection III B above, the vibrational level of the $X - \Pi$ state is only considered in this study, and actually, the H-T interaction has been included as the $g_K$ term. In the present work, we need to treat Sears resonance as a second-order perturbation, and need to include the $F_0$ and $F_2$ parameters derived using the Van Vleck transformation.

B. A remarkable observation of Sears resonance

On the first decimal accuracy of eigen vectors listed in Table IV, four vibronic levels, $(01^0)\mu \Sigma_2^−, (02^0)\mu \kappa \Pi_1^2, (02^0)\mu \kappa \Pi_2^2, (02^0)\mu \kappa \Pi_3^2$, are almost closed within the four basis functions by R-T and Sears interactions.
respectively, because the column and row vectors in the transformation matrix above are almost ortho-normal to each other (e.g., \((+0.4)^2 + (+0.8)^2 + (+0.3)^2 + (-0.2)^2 = 0.93 \approx 1\) and \((0.4) \times (+0.1) + (+0.8) \times (+0.3) + (+0.3) \times (-0.8) + (-0.2) \times (+0.4) = -0.04 \approx 0\), the four-to-four transformation is close within the 4D linear space; in other words, the four vibronic levels are completely expressed within the four bases. The four vibronic levels are shown in Fig. 9. The square-sums for the highest level, \(|(02^00) \kappa \, 2\Pi_\frac{1}{2}\rangle\), have the largest deviation from 1.0, i.e., \(0.89 = (-0.5)^2 + (-0.8)^2\), among the four. This is thought to be natural because this highest level is the closest to other higher-lying levels than the other three, and thus the interaction strength of this highest level is expected to be larger than the others. In the \(4 \times 4\) transformation matrix above, the two \(2 \times 2\) matrices at the diagonal left-upper and right-lower positions, as indicated below, mainly describe R-T interaction at the \((01^10) \Sigma\) and \((02^00) \Sigma\) levels, respectively,

\[
\begin{pmatrix}
0.9 & -0.4 & 0.0 & 0.0 \\
0.4 & 0.8 & 0.3 & -0.2 \\
0.1 & 0.3 & -0.8 & 0.4 \\
0.0 & 0.0 & -0.5 & -0.8 \\
\end{pmatrix},
\]

and the R-T interactions at the \((02^00) \Sigma\) and \((01^10) \Sigma\) levels are extracted from Eq. (2) as follows:

\[
\begin{pmatrix}
| (01^10) \mu \Sigma(-) \rangle \\
| (01^10) \kappa \Sigma(+ \rangle \\
\end{pmatrix} = \begin{pmatrix}
0.9 & -0.4 \\
0.4 & 0.8 \\
\end{pmatrix}\begin{pmatrix}
| - \rangle + \frac{1}{2} | 0; 1, +1 \rangle \\
| + \rangle + \frac{1}{2} | 0; 1, -1 \rangle \\
\end{pmatrix} + \begin{pmatrix}
0.1 & -0.1 \\
-0.2 & 0.0 \\
\end{pmatrix}\begin{pmatrix}
| - \rangle + \frac{1}{2} | 0; 1, -1 \rangle \\
| + \rangle + \frac{1}{2} | 0; 1, +1 \rangle \\
\end{pmatrix}
\]

and

\[
\begin{pmatrix}
| (02^00) \mu \Sigma(-) \rangle \\
| (02^00) \kappa \Sigma(+ \rangle \\
\end{pmatrix} = \begin{pmatrix}
-0.8 & 0.4 \\
-0.5 & -0.8 \\
\end{pmatrix}\begin{pmatrix}
| + \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
| - \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
\end{pmatrix} + \begin{pmatrix}
-0.1 & 0.2 \\
0.1 & 0.0 \\
\end{pmatrix}\begin{pmatrix}
| + \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
| - \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
\end{pmatrix},
\]

where components of the \(v_2 = 3\) and \(=4\) levels are added to the equations of the \(\Sigma\) and \(\Pi\) levels, respectively, which are not listed in Table IV, because none of the contributions is >10%, but in the supplementary material. R-T has two types of interactions, \(\Delta \nu_2 = 0\) and \(\pm 2\),

\[\langle K; \tau; v_2 \mid H_{\text{RT}} \mid K; \pm; v_2 \rangle = \frac{1}{2} \epsilon \omega_2 [(\bar{v}_2 \pm K)(\bar{v}_2 - K)]^\frac{1}{2},\]

where \(H_{\text{RT}}\) is the R-T Hamiltonian, \(\pm\) or \(\tau\) in the wavefunctions expresses \(\Lambda (\pm 1,\ \text{because of the } \Sigma^\frac{1}{2}\text{ electronic state}),\) and \(\bar{v}_2 = v_2 + 1\). In Eqs. (4) and (5), the off-diagonal elements of the first and second terms indicate the \(\Delta \nu_2 = 0\) and \(\pm 2\) contribution, respectively, of the R-T. The coefficients in the equations clearly show that the R-T mixes the components of \(\pm \Lambda\) with \(\Delta \nu_2 = 0\) and also those with \(\pm 2\). Generally, two-to-two transformation is expressed using a rotation matrix as follows:

\[
\begin{pmatrix}
| \mu \rangle \\
| \kappa \rangle \\
\end{pmatrix} = \begin{pmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta \\
\end{pmatrix}\begin{pmatrix}
| - \rangle \\
| + \rangle \\
\end{pmatrix},
\]

and the rotation matrix shows strength of the mixing, e.g., when \(\theta = 45^\circ\), 50% mixing between two bases, \(| - \rangle\) and \(| + \rangle\), is expressed. The first terms of Eqs. (4) and (5) show that, neglecting the contributions less than 10%, i.e., neglecting the second terms, the R-T mixing with \(\Delta \nu_2 = 0\) is close to one-to-one mixing with 2:1; e.g.,

\[
| (01^10) \mu \Sigma(-) \rangle \approx \frac{2}{\sqrt{5}} | - \rangle + \frac{1}{2} | 0; 1, +1 \rangle - \frac{1}{\sqrt{5}} | + \rangle + \frac{1}{2} | 0; 1, -1 \rangle.
\]

The off-diagonal elements, left-lower and right-upper, of the transformation matrix in Eq. (2) indicate Sears resonance. As shown in matrix (3), the upper and lower two elements in the left-lower and right-upper parts, respectively, are remarkable, while the lower and upper ones in the two parts, respectively, are negligible on the present first decimal accuracy. Thus, this shows a typical example of Sears resonance with an almost one-to-one mixing between the two levels, \((01^10) \kappa \Sigma^\frac{1}{2}\) and \((02^00) \mu \Pi^\frac{1}{2}\), with \(\Delta K = \pm 1\) and \(\Delta P = 0\). For Eq. (2), the contributions of the four bases to the two \(\Sigma\) and \(\Pi\) levels can be marked with underline as follows:

\[
\begin{pmatrix}
| (01^10) \mu \Sigma(-) \rangle \\
| (01^10) \kappa \Sigma(+ \rangle \\
| (02^00) \mu \Sigma(-) \rangle \\
| (02^00) \kappa \Sigma(+ \rangle \\
\end{pmatrix} = \begin{pmatrix}
0.9 & -0.4 & 0.0 & 0.0 \\
0.4 & 0.8 & 0.3 & -0.2 \\
0.1 & 0.3 & -0.8 & 0.4 \\
0.0 & 0.0 & -0.5 & -0.8 \\
\end{pmatrix}\begin{pmatrix}
| - \rangle + \frac{1}{2} | 0; 1, +1 \rangle \\
| + \rangle + \frac{1}{2} | 0; 1, -1 \rangle \\
| + \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
| - \rangle - \frac{1}{2} | 1; 2, 0 \rangle \\
\end{pmatrix},
\]
and

\[
\begin{pmatrix}
(01^0)\mu \Sigma^- \\
(01^0)\kappa \Sigma^+ \\
(20^0)\mu \Pi_1^2 \\
(20^0)\kappa \Pi_1^2 \\
\end{pmatrix} =
\begin{pmatrix}
0.9 & -0.4 & 0.0 & 0.0 \\
0.4 & 0.8 & 0.3 & -0.2 \\
0.1 & 0.3 & -0.8 & 0.4 \\
0.0 & 0.0 & -0.5 & -0.8 \\
\end{pmatrix}
\begin{pmatrix}
|+\rangle + \frac{1}{2}|0; 1, +1\rangle \\
|+\rangle + \frac{1}{2}|0; 1, -1\rangle \\
|+\rangle - \frac{1}{2}|1; 2, 0\rangle \\
|+\rangle - \frac{1}{2}|1; 2, 2\rangle \\
\end{pmatrix},
\]

for the \(\Sigma\) and \(\Pi\) levels, respectively. As shown in Table I, among the four bases, there are three types of Sears resonance: (1) \(\Delta\Lambda = 0\) at \(\Lambda = -1\), (2) \(\Delta\Lambda = 0\) at \(\Lambda = 1\), and (3) \(\Delta\Lambda = \pm 2\) at \(\Lambda = \pm 1\). The 0.3 component in both levels and the 0.1 component in the \(\Pi\) level correspond to the first and third types above, respectively, and the -0.2 component in the \(\Sigma\) level is forbidden in the Sears resonance. From the four dimensional eigen vectors for the \(\Sigma\) and \(\Pi\) levels with elements underlined above, it is realized that they have \(|+\rangle + \frac{1}{2}|0; 1, -1\rangle\) and \(|+\rangle - \frac{1}{2}|1; 2, 2\rangle\), respectively, as the major component, and have the others as the minor ones. The two minor components in the off-diagonal parts of the matrix, Eq. (3), are comparable with that in the diagonals, e.g., those in the off-diagonal matrix, 0.1 and 0.3, of the \((20^0)\mu \Sigma^+ \Pi_1^2\) level are comparable with the diagonal, 0.4, and thus it is thought that this shows comparable contribution of Sears resonance with R-T on these four vibronic levels.

The four-to-four transformation within the 4D linear space, Eq. (2), agrees with those obtained from computational studies\(^{30}\) (though the computational study does not give phase of coefficients),

\[
\begin{pmatrix}
(01^0)\mu \Sigma^- \\
(01^0)\kappa \Sigma^+ \\
(20^0)\mu \Pi_1^2 \\
(20^0)\kappa \Pi_1^2 \\
\end{pmatrix} =
\begin{pmatrix}
0.92 & 0.35 & 0.11 & 0.09 \\
0.39 & 0.85 & 0.32 & 0.14 \\
0.11 & 0.38 & 0.81 & 0.43 \\
0.00 & 0.00 & 0.54 & 0.84 \\
\end{pmatrix}
\begin{pmatrix}
|+\rangle + \frac{1}{2}|0; 1, +1\rangle \\
|+\rangle + \frac{1}{2}|0; 1, -1\rangle \\
|+\rangle - \frac{1}{2}|1; 2, 0\rangle \\
|+\rangle - \frac{1}{2}|1; 2, 2\rangle \\
\end{pmatrix},
\]

for even and odd parities (this parity is interpreted as that on \(K\), i.e., \(\frac{1}{\sqrt{2}}[|+K\rangle \pm |-K\rangle]\), in the present analysis), respectively.

It is thought that, because the four vibronic levels considered here are low-lying vibronic levels and thus contamination by the other higher levels to them is expected to be relatively small, the four-to-four mixing is quite natural. This is also one of the reasons for the good agreement of the computational result. This Sears resonance between the non-unique levels discussed here corresponds to that observed between \((02^0)\mu^2 \Sigma^+ \Pi_1^2\) and \((01^0)^2 \Delta_2^0\), i.e., between the non-unique and unique levels, respectively, in NCS,\(^{27}\) in which the present and NCS cases are regular and inverted, respectively.

C. The constant of Sears resonance

As mentioned in Subsection III B, He et al. suggested that there are two kinds of Sears resonance parameters, \(F\), for \(\Delta\Lambda = 0\) and \(\pm 2\),\(^{28}\) and that the latter has an additional factor 2 than the former under the limited situation where only \(\Sigma\) states interact with \(\Pi\). Although they did not mention how to generate the additional factor 2, we have confirmed the existence of the factor 2.\(^{34}\) As shown in Table III, \(F_0\) and \(F_2\) obtained for the \(\bar{X}\) \(\Pi\) state of SiCN in the present analysis barely show this factor 2 relation, \(F_2/F_0 = 7.8/4.9 = 1.6\). As discussed in our previous work\(^{12}\) and the other computational works,\(^{8,9}\) it is predicted that there are \(2\Sigma^+\) and \(2\Sigma^-\) excited states near the \(\bar{A}\) \(2\Delta\) state. Thus the factor 2 relation had not been expected in the present SiCN system, because the factor 2 is expected under the limited situation considering only \(\Sigma\) states as the perturbers. It is thought that the factor obtained in the present SiCN system is just one generated accidentally, due to sum of the effects by the three excited states, \(\Sigma^+, \Sigma^+, \Sigma^-\), and \(2\Delta\). Understanding of the Sears resonance constants, \(F_0\) and \(F_2\), from the view of computational studies is expected to be very interesting.

It is thought that the similar consideration for the Sears constants above can be applied to the H-T constant of the present SiCN system mentioned in Subsection III B. H-T interaction has selection rule, \(\Delta \Lambda = \pm 1\) and \(\Delta l = \mp 1\), and thus \(\Delta K = 0\) (\(K = L + I\)),\(^{25}\) and hence the \(\bar{X}\) \(2\Pi\) state can also interact with the three excited states, \(2\Sigma^+, 2\Sigma^-, \text{ and } 2\Delta\). The apparent negligible constant of \(g_K\) listed in Table III may be caused by accidental cancellation among the constants of the \(2\Pi\) state with the three states. The opposite sign of the \(g_K\) constants of a \(4\Pi\) state coupling with \(2\Sigma\) and \(2\Delta\) is suggested.\(^{25}\)

He and Clouthier systematically discussed Sears resonance.\(^{35,37}\) In their discussion, it is said that the \(F_0\) term consists of the electron spin-vibrational angular momentum coupling, which is the first-order interaction by the \(S_0 q^T\) term in their notation, i.e., the first term of the right-hand-side of their Eq. (46). In contrast, Sears resonance has been defined as the second-order interaction in a \(\Pi\) electronic state through \(\Sigma\) and/or \(\Delta\) states, using the \(S_0 L \perp L_\perp q^T\) term.\(^{27}\) Although it is impossible to remarkably distinguish the first- and second-order interactions on analysis of the observed spectrum practically, we think it should not be \(S_0 q^T\), but should be \(S_0 L \perp L_\perp q^T\) according to the definition. It is expected that...
the first-order electron spin-vibrational angular momentum coupling is relatively small, and it is comparable with the strength of $\Lambda$-type doubling. Actually it is observed in a rotational spectrum in the $\tilde{X}$ $^2\Pi$ state of CsH.\textsuperscript{38} We have also observed this coupling in the rotational structure of the vibronic band of the $\tilde{A}$ $^4\Pi$–$\tilde{X}$ $^2\Sigma$ transition of MgNC as a $P$-type doubling of a $\Pi$ vibronic level caused by coupling with a $\Sigma$ level lying closely.\textsuperscript{39}

D. Chaotic characteristics of the $\tilde{X}$ $^2\Pi$ state of SiCN

The species showing Sears resonance, which have been reported so far, are listed in Table V. In the works on the species reported previously, any difficulties on their vibrational assignments have not been proposed, while, as mentioned in Subsection III C above, we have the difficulty on the assignment of the vibrational quantum number for the vibrational levels of the $\tilde{X}$ $^2\Pi$ state of SiCN; in other words, in view of the 2D-HO basis, we have met chaotic appearance in some of the vibrational levels, though the levels have been expressed as the eigen states for the vibronic Hamiltonian adopted in the present numerical analysis. Except the R-T parameter, $\epsilon$, all of the molecular constants of the $\tilde{X}$ $^2\Pi$ state of SiCN are moderate among the species listed in Table V. Even for $\epsilon$, although that of SiCN is more than twice of that of NCS, the constants, $\epsilon \omega_2$, are comparable for the two species, where the R-T parameter, $\epsilon$, actually affects the R-T interaction as the latter constant, $\epsilon \omega_2$. In addition, although the value, $\epsilon = 0.3393$, is close to the limit which can adopt perturbation treatment,\textsuperscript{40} it is still within the limit. As seen from Table V, for the species studied previously, it is thought that Sears resonance may be induced from the relatively large effect on the SO and H-T interactions indicated by the $A$ and $g_K$ constants, respectively, because Sears resonance is the second-order interaction between the two interactions. In contrast, for SiCN, the H-T interaction is almost negligible, while the SO and Sears couplings are considerable, though the negligible $g_K$ would be caused from accidental cancellation, as discussed in Subsection IV C. It can be therefore said that none of the interactions of SiCN are strong among the species, but are moderate. Accordingly, it is concluded that the chaotic characteristics of the vibrational structure, appearing even at $\sim$1000 cm$^{-1}$, are induced from the complex and accidental proximities of the levels caused by R-T, Fermi, and Sears interactions rather than from strong interaction.

The barrier of isomerization reaction, SiCN $\rightleftharpoons$ SiNC is predicted to be $\sim$7000 cm$^{-1}$\textsuperscript{7,9,10} The bending and Si-CN stretching vibrational modes are thought to be effective for the isomerization reaction as discussed in our MgNC work.\textsuperscript{31} Because the chaotic appearance identified in this work is a mixing between the two modes, it is thought that this observation indicates the trace of the beginning for the isomerization reaction and a correlation of the chaotic vibrational levels to the transition state for the isomerization reaction. This observation also indicates that electron spin may be effective for the isomerization in some cases, because Sears resonance is needed for the analysis of the chaotic appearance observed in the present SiCN/SiNC system.

E. Evaluation of derivatives for parameter optimization

In the non-linear least square fitting procedure, we used iterative procedure of Newton method,\textsuperscript{42} and to calculate derivative matrix, the so-called Jacobian (matrix), we adopted Hellmann-Feynman theorem or numerical differentiation. Practically, we feel that the Jacobian derived from the Hellmann-Feynman theorem is inefficient in converging for the present vibronic Hamiltonian, though we have experiences that actually the Hellmann-Feynman theorem is very efficient for a more precise (finer) situation, such as rotational analyses. We thus adopted the numerical differentiation procedure to calculate the Jacobian in the present numerical analysis. This procedure is more efficient for the converging than the Hellmann-Feynman theorem, though this is very inefficient to calculate the Jacobian, because it is needed to numerically solve the eigen-value problem at least twice for each iterative routine for the trial parameters (actually we calculated it three times, because our derivatives are calculated as $\sum_j \frac{\partial}{\partial p_i} E_j = \frac{1}{2 \pi r} \{ f(p_i + \Delta h_i) - f(p_i - \Delta h_i) \}$, where $\frac{\partial}{\partial p_i} E_j$, $p_i$, and $\Delta h_i$ are a numerical derivative of the $j$th level energy by the $i$th parameter, the trial value, and incremental difference for the $i$th parameter, respectively). Principally, the Hellmann-Feynman theorem is only effective in a “real” system, which corresponds to be established on the system converged. In the present case, because of vibrational analysis with accuracy of a few cm$^{-1}$, the trial parameters are a bit too far from the true values and the system is also far from its “real” situation, and it is thus thought that derivatives derived from the Hellmann-Feynman theorem would not be appropriate. Although convinced reason is not clear at present, this would be one of the reasons for inappropriate procedure of Hellmann-Feynman theorem for the present treatment.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\omega_2$ (cm$^{-1}$)</th>
<th>$\epsilon$</th>
<th>$\omega_3$ (cm$^{-1}$)</th>
<th>$W_1$</th>
<th>$A$</th>
<th>$g_K$</th>
<th>$F$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS</td>
<td>$\tilde{X}$ $^2\Pi$</td>
<td>375.96</td>
<td>−0.1598</td>
<td>735.41</td>
<td>15.71</td>
<td>1.86</td>
<td>−327.59</td>
<td>2.24</td>
</tr>
<tr>
<td>GeCH</td>
<td>$\tilde{X}$ $^2\Pi$</td>
<td>434.8</td>
<td>0.0262</td>
<td>831.3</td>
<td>7.252</td>
<td>…</td>
<td>−383.8</td>
<td>10.31</td>
</tr>
<tr>
<td>GeCD</td>
<td>$\tilde{X}$ $^2\Pi$</td>
<td>334.1</td>
<td>0.0143</td>
<td>816.2</td>
<td>…</td>
<td>…</td>
<td>−383.0</td>
<td>7.53</td>
</tr>
<tr>
<td>SiCN</td>
<td>$\tilde{X}$ $^2\Pi$</td>
<td>246.74</td>
<td>0.3393</td>
<td>584.3</td>
<td>14.046</td>
<td>4.31</td>
<td>114.2</td>
<td>−0.18</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Value evaluated from $\epsilon \omega_2$ and $\epsilon \omega_3$.
\textsuperscript{b}Constants with $\epsilon > 0$.
\textsuperscript{c} $P_1$ and $P_2$, respectively.

This work
SUPPLEMENTARY MATERIAL

See supplementary material for all of the eigen values and the coefficients of the basis functions for the eigen state, i.e., the elements of the eigen vectors, derived in the present numerical analysis.

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23T. C. Smith, H. Li, D. A. Hostutler, D. J. Cloutier, and A. Merer, J. Chem. Phys. 114, 725 (2001); there are misprints in Eqs. (7) and (8) and Fig. 2 of the paper; (vI + 1) in Eqs. (7) and (8) should be vI. For Fig. 2, because the matrix elements of the anharmonic terms are independent upon SO, we have two separate matrixes with the different diagonal elements, D1 or D2 in their notation, for two Σ components, and all of the diagonal elements in each matrix for Σ should be the same, as mentioned on the 3rd step of our analysis code in the text.
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34M. Fukushima, “Note on the matrix elements of Sears resonance” (unpublished).
35S.-G. He and D. J. Cloutier, J. Chem. Phys. 123, 014316 (2005), He and Cloutier proposed a computer program, RT3, to analyze the bending structure affected by R-T effect.36 We have also confirmed RT3 works very well for our 3rd step, though the 4th and 5th steps do not agree. Very recently, RT3 is also tested for the analysis of the ˜X 2H state of CCN,37 which is within our 3rd step.