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Two-vibron excitations in the ferroelectric phase of NaNO_2

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In relation with recently observed overtone spectra for the ferroelectric phase of solid NaNO_2 , we have performed lattice-dynamics calculations. From a basis of single-vibron functions computed in a previous paper and including both the intramolecular and intermolecular anharmonicity, we have calculated the two-vibron states and the Raman and luminescence intensities. Good agreement with the different experimental spectra was obtained for an intramolecular anharmonicity constant $A = 1.3 \text{ cm}^{-1}$. We conclude that the line shapes in the luminescence and Raman spectra are determined by the occurrence of a quasibound bivibron state which is weakly coupled to the two-vibron states.

I. INTRODUCTION

Solid NaNO_2 is an interesting molecular ionic crystal which is extensively studied. Recently, Kato *et al.*¹ measured Raman scattering and singlet and triplet luminescence spectra of the overtones of the ν_2 vibration in the ferroelectric phase of NaNO_2 . In these spectra they found unexpected sharp peaks embedded in broad multivibron bands. They concluded that a quasibound two-vibron state was formed with an anharmonicity parameter of $0.8 \pm 0.5 \text{ cm}^{-1}$ and that the higher vibron states are truly bound. In this paper we investigate by means of lattice-dynamics calculations whether there is indeed a quasibound two-vibron state and we compare our results with the experimental spectra.

The ν_2 vibration corresponds to an internal bending mode of the nitrite ions. If a vibration in the crystal is purely harmonic, the excitation energy of a doubly excited state will be exactly twice the excitation energy of the fundamental state. For vibrons this means that there is no difference between the excitation energy of two fundamental vibrons traveling independently through the crystal (a two-vibron state) and a vibron in which each molecule is doubly excited (an overtone state). But if the molecular vibration is anharmonic and the energy of the doubly excited vibration is lower than twice the fundamental excitation energy, there are different possibilities. If the anharmonicity is large compared with the vibron bandwidth, a bivibron state can be formed in which an overtone vibration travels through the crystal. This state is sometimes called a bound state and has little coupling to the states in the two-vibron band. If the anharmonicity is small, there is a strong coupling between the overtone and two-vibron states. The energy of the overtone lies in the two-vibron band, and no bivibron is formed. The theory of bivibron states was developed by Agranovich and Lalov,² Belousov,³ and Agranovich, Dubovski, and Orlov⁴⁻⁶ and others.⁷⁻⁹ Experimental two-vibron spectra are reported for a number of crystals which contain small molecules such as NH_4^+ , CO_3^{2-} , NO_3^- , CO_2 , N_2O , and OCS .¹⁰⁻¹³ Other theoretical calculations on two-vibron spectra have been performed by Dows and Schettino¹⁰ for CO_2 and by Bogani⁹ for CO_2 , N_2O , and OCS .

In a previous paper¹⁴ we have calculated the fundamental phonon and vibron states of the NaNO_2 crystal. In these calculations the intermolecular interactions were modeled by a semiempirical atom-atom potential supplemented with point charges and the molecular polarizabilities were included by the shell model. The results were in fairly good agreement with the experimental data. In the calculations presented here, we used the same model potential and calculated the single-vibron states as in the previous paper. The structure of the ferroelectric phase of NaNO_2 is also described in that paper.

II. THEORY

A. Two-vibron states

For the derivation of the expressions needed for the calculation of the two-vibron energies in the crystal, we used the same ansatz and notation as Agranovich,¹⁵ but follow a different route. In second quantization we write the harmonic crystal Hamiltonian for one internal vibration as

$$H_0 = \sum_n \Omega B_n^\dagger B_n + \sum_{n,m}' V_{nm} B_n^\dagger B_m, \quad (1)$$

where Ω is the excitation energy of the free molecular vibration, B_n^\dagger and B_n are the excitation and deexcitation operators for the molecular vibration on the molecule with position vector \mathbf{n} , and V_{nm} is the coupling between the excitations on molecules \mathbf{n} and \mathbf{m} . Because of the translational symmetry in the crystal, we can Fourier transform the molecular excitation operators to crystal excitation operators

$$B_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_n B_n \exp(-i\mathbf{k}\cdot\mathbf{n}), \quad (2)$$

$$B_{\mathbf{k}}^\dagger = \frac{1}{\sqrt{N}} \sum_n B_n^\dagger \exp(i\mathbf{k}\cdot\mathbf{n}),$$

where \mathbf{k} is a vector in the first Brillouin zone and N is the number of unit cells in the crystal. The crystal Hamiltonian can now be written as

$$H_0 = \sum_{\mathbf{k}} [\Omega + V(\mathbf{k})] B_{\mathbf{k}}^\dagger B_{\mathbf{k}}, \quad (3)$$

with

$$V(\mathbf{k}) = \sum_{\mathbf{m} (\neq \mathbf{n})} V_{\mathbf{nm}} \exp[i\mathbf{k} \cdot (\mathbf{m} - \mathbf{n})]. \quad (4)$$

The eigenfunctions of this Hamiltonian are the vibrons which can be labeled by \mathbf{k} and can be written as

$$|1_{\mathbf{k}}\rangle = B_{\mathbf{k}}^{\dagger} |0\rangle, \quad (5)$$

with energy

$$\epsilon_{\mathbf{k}} = \Omega + V(\mathbf{k}). \quad (6)$$

The anharmonicity in the crystal is introduced in two different ways. First, there is the intramolecular anharmonicity that is included by the operator

$$H_a = -A \sum_{\mathbf{n}} (B_{\mathbf{n}}^{\dagger})^2 B_{\mathbf{n}}^2, \quad (7)$$

where A is defined as the difference between the fundamental molecular excitation energy and half of the excitation energy of the doubly excited state. It can be shown that if the intramolecular anharmonicities of third and fourth order are taken into account by means of a contact transformation⁸, we obtain a Hamiltonian of the form $H = H_0 + H_a$. The intermolecular anharmonicity is introduced by

$$H_t = \frac{1}{2} \sum'_{\mathbf{n}, \mathbf{m}} W_{\mathbf{nm}} (B_{\mathbf{n}}^{\dagger})^2 B_{\mathbf{m}}^2, \quad (8)$$

where $W_{\mathbf{nm}}$ describes the interaction between the doubly excited states on the molecules \mathbf{n} and \mathbf{m} . By the use of Eq. (2), we can write Eqs. (7) and (8) as

$$H_a + H_t = - \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\mathbf{k}''} \frac{A - \frac{1}{2} W(\mathbf{k} + \mathbf{k}')}{N} \times B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}'}^{\dagger} B_{\mathbf{k}} B_{\mathbf{k}'} B_{\mathbf{k}''} B_{\mathbf{k} + \mathbf{k}' - \mathbf{k}''}, \quad (9)$$

with

$$W(\mathbf{k}) = \sum_{\mathbf{m} (\neq \mathbf{n})} W_{\mathbf{nm}} \exp[i\mathbf{k} \cdot (\mathbf{m} - \mathbf{n})]. \quad (10)$$

We want to obtain the two-vibron states and energies, and so we have to diagonalize the total Hamiltonian $H = H_0 + H_a + H_t$ in a basis of harmonic two-vibron states. These can be written as

$$|2_{\mathbf{k}\mathbf{k}'}\rangle = B_{\mathbf{k}}^{\dagger} B_{\mathbf{k}'}^{\dagger} |0\rangle. \quad (11)$$

Because these states contain two crystal excitations, they can be labeled by two independent wave vectors. The matrix elements of the Hamiltonian are easily calculated:

$$\langle 2_{\mathbf{q}\mathbf{q}'} | H | 2_{\mathbf{k}\mathbf{k}'} \rangle = \delta(\mathbf{q} + \mathbf{q}' - \mathbf{k} - \mathbf{k}') \times \left[\delta(\mathbf{q} - \mathbf{k})(\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}'}) - \frac{2A - W(\mathbf{k} + \mathbf{k}')}{N} \right]. \quad (12)$$

From the first δ function, it is clear that only two-vibron states with equal total wave vector are mixed. Therefore, the Hamiltonian (12) can be diagonalized separately for

each wave vector $\mathbf{K} = \mathbf{k} + \mathbf{k}'$. The structure of the Hamiltonian is extremely simple; it can be considered as the sum of a diagonal matrix and a constant matrix.

The formal solution for the eigenstates of this Hamiltonian is given by Agranovich¹⁵ by the use of the Green's-function method. The two-vibron Green's function for a given \mathbf{K} contains an integration over the first Brillouin zone. Since this integration over \mathbf{k} cannot be performed analytically, it is replaced by a summation over a grid of \mathbf{k} points. This is equivalent to the diagonalization of the Hamiltonian in Eq. (12), where \mathbf{k} runs over this grid. For convergence, the number of points, and thus the dimension of the matrix, must become very large. Standard diagonalization routines are too slow and too storage intensive for solving this eigenvalue problem. But because of the special structure of the Hamiltonian, a simple diagonalization scheme can be used. In matrix form the Hamiltonian can be written as

$$\underline{H}(\mathbf{K}) = \underline{D}(\mathbf{K}) + \underline{C}(\mathbf{K}), \quad (13)$$

where $\underline{D}(\mathbf{K})$ is the diagonal matrix with elements

$$D_{\mathbf{q}\mathbf{k}}(\mathbf{K}) = \delta_{\mathbf{q}\mathbf{k}}(\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}) \quad (14a)$$

and $\underline{C}(\mathbf{K})$ is the constant matrix

$$C_{\mathbf{q}\mathbf{k}}(\mathbf{K}) = c = \frac{-2A + W(\mathbf{K})}{N}. \quad (14b)$$

We omit the \mathbf{K} dependence of the matrices and write \underline{C} as

$$\underline{C} = c \mathbf{1} \mathbf{1}^T, \quad (15)$$

where $\mathbf{1}$ is a column vector of length N with all elements equal to 1. For a certain eigenvector \mathbf{e}^i , the eigenvalue problem looks like

$$(\underline{D} + c \mathbf{1} \mathbf{1}^T) \mathbf{e}^i = \omega^i \mathbf{e}^i. \quad (16)$$

We now define the scalar α as

$$\alpha = c \mathbf{1}^T \mathbf{e}^i \quad (17)$$

and write the eigenvalue problem of Eq. (16) for row \mathbf{q} as

$$(\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}) e_{\mathbf{q}}^i + \alpha = \omega^i e_{\mathbf{q}}^i. \quad (18)$$

If $\omega^i \neq \epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}$, then the component \mathbf{q} of eigenvector \mathbf{e}^i is given by

$$e_{\mathbf{q}}^i = \frac{\alpha}{\omega^i - (\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}})}. \quad (19)$$

Inserting Eq. (19) into Eq. (17) gives

$$1 = \sum_{\mathbf{q}} \frac{c}{\omega^i - (\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}})}. \quad (20)$$

The eigenvalues ω^i can thus be found as the zeros of the function

$$f(\omega) = \sum_{\mathbf{q}} \frac{c}{\omega - (\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}})} - 1. \quad (21)$$

Equation (20) is the same as Eq. (20a) derived by Agranovich¹⁵ by the use of Green's functions. The function $f(\omega)$ is singular for $\omega = \epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}$, i.e., when the state with en-

ergy ω lies within the two-vibron band. In the Green's-function method, these poles are avoided by adding a small imaginary component to ω . Here we deal with a finite grid of points \mathbf{q} and we use an algorithm that finds ω in a stable manner, even when it coincides with $\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}$ or lies close to such a pole. It can be proved that between every two values of $\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}$ there will be exactly one ω^i which cannot be equal to one of the diagonal elements $\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}}$ unless this element is degenerate.¹⁶ Such a zero of $f(\omega)$ can be found by the Newton-Raphson procedure. If the eigenvalues ω^i are known, the corresponding eigenvectors can be found by the use of Eq. (19), where α is simply the normalization constant of the eigenvector. Next, we consider the case of degenerate diagonal elements. If g is the degeneracy of a given diagonal element, then there are $g-1$ roots ω^i which are exactly equal to this element. In this case it follows from Eq. (18) that $\alpha=0$. From Eq. (17) and the fact that $c \neq 0$, we obtain the following condition for the corresponding eigenvectors:

$$\sum_{\mathbf{q}} e_{\mathbf{q}}^i = 0. \quad (22)$$

For all the components $e_{\mathbf{q}}^i$ with vectors \mathbf{q} for which $\epsilon_{\mathbf{q}} + \epsilon_{\mathbf{K}-\mathbf{q}} \neq \omega^i$, we know from Eq. (19) that $e_{\mathbf{q}}^i = 0$. This is sufficient to determine all the remaining eigenvectors.

B. Luminescence and Raman-scattering intensities

If we want to compare the calculated two-vibron spectra with laser luminescence spectra, we have to calculate the luminescence intensities of the two-vibron transitions. The intensity is proportional to the oscillator strength of the transition: $|\langle f | \boldsymbol{\mu} | i \rangle|^2$, where $|i\rangle$ is the initial state, $|f\rangle$ the final state of the luminescence process, and $\boldsymbol{\mu}$ is the dipole moment operator. In the luminescence experiments of Kato *et al.*,¹ the initial state is an electronically excited state (singlet or triplet) with no vibrations excited:

$$|i\rangle = |1_{\mathbf{k}}^{\text{el}} 0^{\text{vib}}\rangle. \quad (23a)$$

The final state in the luminescence process under consideration is the electronic ground state with a two-vibron state excited:

$$|f\rangle = |0^{\text{el}} 2_{\mathbf{k}}^{\text{vib}}\rangle. \quad (23b)$$

For the electronically excited state, we can assume the exciton model

$$|1_{\mathbf{k}}^{\text{el}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n}) |1_{\mathbf{n}}^{\text{el}}\rangle \prod_{\mathbf{m} (\neq \mathbf{n})} |0_{\mathbf{m}}^{\text{el}}\rangle. \quad (24)$$

The transition dipole moment then becomes

$$\langle f | \boldsymbol{\mu} | i \rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{n}} \exp(i\mathbf{k}\cdot\mathbf{n}) \langle 2_{\mathbf{k}}^{\text{vib}} | \boldsymbol{\mu}_{\mathbf{n}}^{\text{el}} | 0^{\text{vib}} \rangle, \quad (25)$$

where

$$\boldsymbol{\mu}_{\mathbf{n}}^{\text{el}} = \langle 0_{\mathbf{n}}^{\text{el}} | \boldsymbol{\mu}_{\mathbf{n}} | 1_{\mathbf{n}}^{\text{el}} \rangle \quad (26)$$

is the electronic transition dipole moment on molecule \mathbf{n} . The two-vibron states are solutions of Eq. (16):

$$|2_{\mathbf{k}}^{\text{vib}}\rangle = \sum_{\mathbf{q}} e_{\mathbf{q}}^j(\mathbf{K}) B_{\mathbf{q}}^{\dagger} B_{\mathbf{K}-\mathbf{q}}^{\dagger} |0^{\text{vib}}\rangle. \quad (27)$$

The electronic transition dipole moment is expanded up to second order in the normal coordinates of the vibration,

$$\boldsymbol{\mu}_{\mathbf{n}}^{\text{el}} = \mathbf{d}^{(1)} Q_{\mathbf{n}} + \mathbf{d}^{(2)} Q_{\mathbf{n}}^2 + \sum_{\mathbf{m} (\neq \mathbf{n})} \mathbf{d}_{\mathbf{nm}}^{(2)} Q_{\mathbf{n}} Q_{\mathbf{m}}, \quad (28)$$

with

$$\begin{aligned} \mathbf{d}^{(1)} &= \left[\frac{\partial \boldsymbol{\mu}_{\mathbf{n}}^{\text{el}}}{\partial Q_{\mathbf{n}}} \right]_0, \\ \mathbf{d}^{(2)} &= \frac{1}{2} \left[\frac{\partial^2 \boldsymbol{\mu}_{\mathbf{n}}^{\text{el}}}{\partial Q_{\mathbf{n}}^2} \right]_0, \\ \mathbf{d}_{\mathbf{nm}}^{(2)} &= \left[\frac{\partial^2 \boldsymbol{\mu}_{\mathbf{n}}^{\text{el}}}{\partial Q_{\mathbf{n}} \partial Q_{\mathbf{m}}} \right]_0. \end{aligned} \quad (29)$$

We have omitted the label \mathbf{n} for $\mathbf{d}^{(1)}$ and $\mathbf{d}^{(2)}$ because all the nitrite ions in NaNO_2 are equivalent. With the aid of the relation

$$Q_{\mathbf{n}} = \frac{1}{\sqrt{2N}} \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}})^{-1/2} \exp(i\mathbf{k}\cdot\mathbf{n}) (B_{\mathbf{k}} + B_{-\mathbf{k}}^{\dagger}), \quad (30)$$

we can calculate the transition dipole moment in Eq. (25):

$$\begin{aligned} &\langle 0^{\text{el}} 2_{\mathbf{k}}^{\text{vib}} | \boldsymbol{\mu} | 1_{\mathbf{k}}^{\text{el}} 0^{\text{vib}} \rangle \\ &= \frac{\delta(\mathbf{K}-\mathbf{k})}{\sqrt{2N}} \sum_{\mathbf{q}} [e_{\mathbf{q}}^j(\mathbf{K})]^* (\epsilon_{\mathbf{q}} \epsilon_{\mathbf{K}-\mathbf{q}})^{-1/2} \\ &\quad \times [2\mathbf{d}^{(2)} + (\mathbf{d}_{\mathbf{q}}^{(2)} + \mathbf{d}_{\mathbf{K}-\mathbf{q}}^{(2)})^*], \end{aligned} \quad (31)$$

with

$$\mathbf{d}_{\mathbf{q}}^{(2)} = \sum_{\mathbf{m} (\neq \mathbf{n})} \mathbf{d}_{\mathbf{nm}}^{(2)} \exp[i\mathbf{q}\cdot(\mathbf{m}-\mathbf{n})]. \quad (32)$$

From the δ function follows the selection rule that the \mathbf{k} vector is conserved in the luminescence process.

In the calculation of the luminescence intensities, we assumed that the transition dipole moment of the nitrite ion is mainly dependent on the vibration of the molecule itself and is little influenced by the vibrations of the other molecules: $\mathbf{d}^{(2)} \gg \mathbf{d}_{\mathbf{nm}}^{(2)}$. This simplifies Eq. (31), and the oscillator strength now becomes

$$\begin{aligned} &|\langle 0^{\text{el}} 2_{\mathbf{k}}^{\text{vib}} | \boldsymbol{\mu} | 1_{\mathbf{k}}^{\text{el}} 0^{\text{vib}} \rangle|^2 \\ &= \frac{|\mathbf{d}^{(2)}|^2}{N} \left| \sum_{\mathbf{q}} e_{\mathbf{q}}^j(\mathbf{K}) (\epsilon_{\mathbf{q}} \epsilon_{\mathbf{K}-\mathbf{q}})^{-1/2} \right|^2. \end{aligned} \quad (33)$$

The Raman-scattering intensity is proportional to $\sum_{\lambda, \mu} |\langle f | \alpha_{\lambda\mu} | i \rangle|^2$, where $\alpha_{\lambda\mu}$ are the components of the unit-cell polarizability tensor. In the scattering process observed by Kato *et al.*,¹ the initial state is the vibrational ground state and the final state is a two-vibron state with $\mathbf{K}=0$. In order to calculate the scattering intensities, we can expand the polarizability in the same manner as the transition dipole moment in Eq. (28). The final expression that we obtain for $\sum_{\lambda, \mu} |\langle f | \alpha_{\lambda\mu} | i \rangle|^2$ is identical to the right-hand side of Eq. (33) with $\mathbf{K}=0$. In this case

$d^{(2)}$ is replaced by the sum over the second derivatives of the components of the polarizability tensor with respect to the normal coordinate of the ν_2 vibration and we have again neglected the contributions of the other molecules.

III. COMPUTATIONAL ASPECTS

The vibron energies ϵ_q that form the diagonal elements of the two-vibron Hamiltonian in Eq. (12) are calculated as described in a previous paper.¹⁴ We have used the atom-atom potential which was developed by Lynden-Bell, Impey, and Klein in molecular-dynamics calculations on solid NaNO_2 .¹⁷ It has an exponential short range and an r^{-6} dispersion contribution, and the electrostatic interactions are modeled by point charges. For the intramolecular potential of the nitrite ion, we used the force field of Weston and Brodasky¹⁸ developed for the nitrite ion in crystalline NaNO_2 . In order to obtain the correct LO-TO splittings of the fundamental vibrons, we adjusted the transition dipole moments of the vibron modes. The polarizability of the ions was taken into account by means of the shell model.^{19,20} Each atom consists of a core that contains the total mass and a massless shell that follows the core motions adiabatically. The interaction between the core and shell is parametrized by a force constant which is related to the atomic polarizabilities. From our calculations in the previous paper,¹⁴

where all the molecular degrees of freedom were taken into account simultaneously, it was clear that the coupling between the ν_2 vibron and other vibrons and lattice vibrations is very small and can be neglected. Therefore, in these calculations, only the ν_2 bending mode of the nitrite ion is considered.

The interaction between the doubly excited states on the molecules \mathbf{n} and \mathbf{m} is given by

$$W_{nm} = \langle 2_n 0_m | V | 0_n 2_m \rangle, \quad (34)$$

where V is the crystal potential and $|2_n\rangle$ is the doubly excited molecular ν_2 vibration on molecule \mathbf{n} . If we make a Taylor expansion of the crystal potential up to fourth order in the normal coordinates of the molecular vibration and apply the well-known rules for matrix elements of harmonic-oscillator functions, we obtain

$$W_{nm} = \frac{1}{8\Omega^2} \left[\frac{\partial^4 V}{\partial Q_n^2 \partial Q_m^2} \right]_0. \quad (35)$$

The atomic displacements are related to the normal coordinates by the eigenvectors l of the molecular vibration,

$$u_{\lambda\alpha n} = l_{\lambda\alpha} Q_n, \quad (36)$$

where α labels the atoms in molecule \mathbf{n} and λ the cartesian directions. If we consider the crystal potential as the sum of atom-atom potentials we obtain for Eq. (35)

$$W_{nm} = \frac{1}{8\Omega^2} \sum_{\alpha,\beta} \sum_{\lambda,\lambda'} \sum_{\mu,\mu'} \left[\frac{\partial^4 V_{n\alpha m\beta}}{\partial u_{\lambda\alpha n} \partial u_{\lambda'\alpha n} \partial u_{\mu\beta m} \partial u_{\mu'\beta m}} \right]_0 l_{\lambda\alpha} l_{\lambda'\alpha} l_{\mu\beta} l_{\mu'\beta}, \quad (37)$$

where $V_{n\alpha m\beta}$ is the interaction between atom α of molecule \mathbf{n} and atom β of molecule \mathbf{m} . For the calculation of W_{nm} , we have used the same atom-atom potential as in the calculations of the fundamental excitations. Although the atom-atom potential contains Coulomb interactions between point charges, we take the fourth derivative of this potential and there are no $0 \rightarrow 2$ transition dipoles. So there will be no LO-TO splitting of the two-vibron levels. Experimentally, this splitting has not been observed either.¹

For the calculation of the two-vibron energies for $\mathbf{K}=\mathbf{0}$, we have used a basis of 18413 harmonic two-vibron functions (\mathbf{q} points). For the total density of two-vibron states and the luminescence spectrum induced by broadband excitation, a further integration over the Brillouin zone has to be performed. This was done by the application of the quadratic integration scheme developed by Wiesenekker, te Velde, and Baerends,^{21,22} using 50 \mathbf{K} points. In this case the energies in every \mathbf{K} point were calculated with a basis of 2411 harmonic two-vibron functions.

IV. RESULTS AND DISCUSSION

First, we have calculated the two-vibron spectra for $\mathbf{K}=\mathbf{0}$. From the diagonalization of the two-vibron Hamiltonian results a continuous band of eigenvalues and no

bound bivibron state is split off. In Fig. 1 we have plotted the number of eigenvalues as a function of the energy for $\mathbf{K}=\mathbf{0}$. This $\mathbf{K}=\mathbf{0}$ density of states in Fig. 1 was calculated using an anharmonicity constant A of 0.8 cm^{-1} as estimated by Kato *et al.* from luminescence spectra.¹

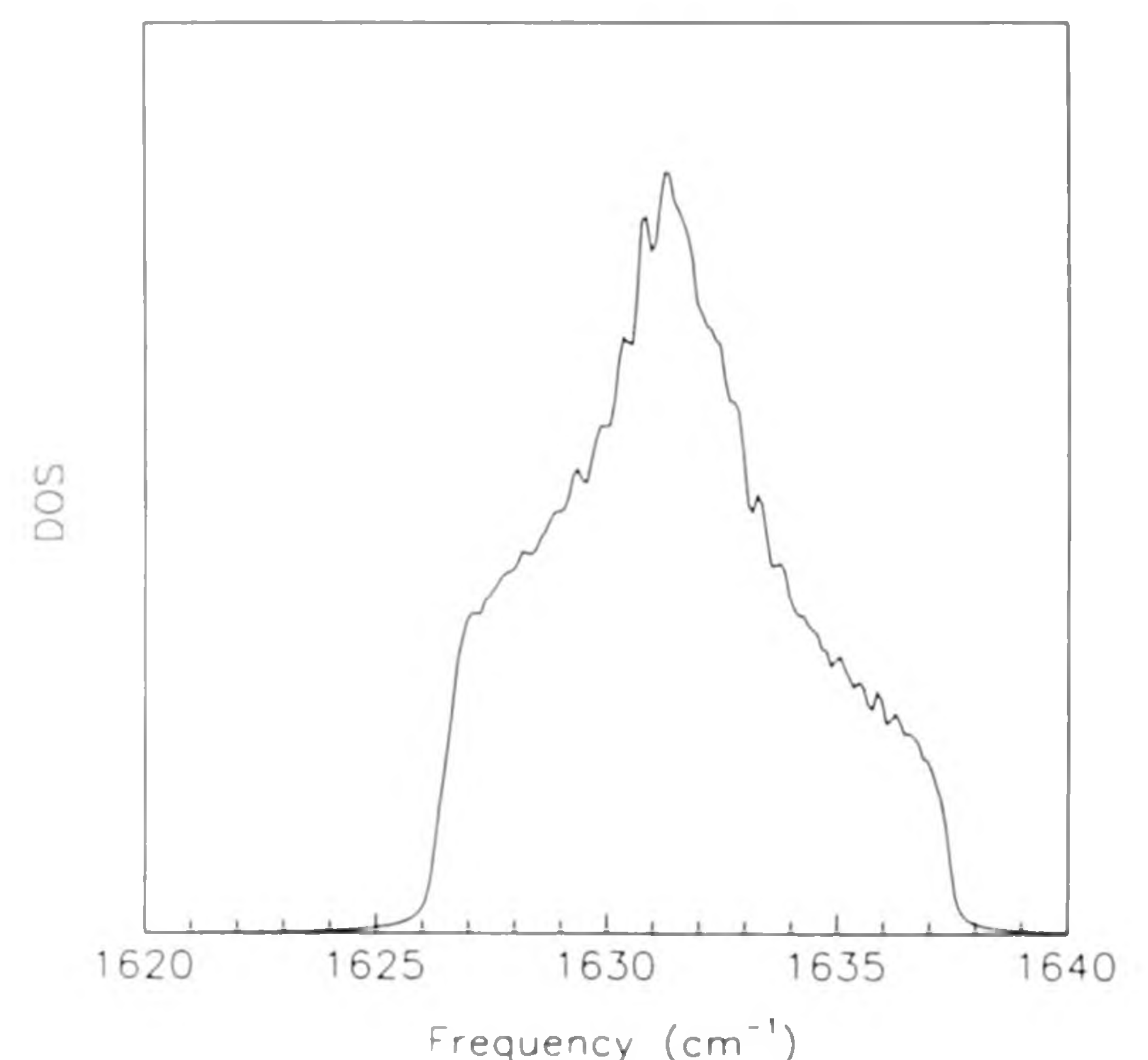


FIG. 1. Density of two-vibron states for $\mathbf{K}=\mathbf{0}$ and $A=0.8 \text{ cm}^{-1}$.

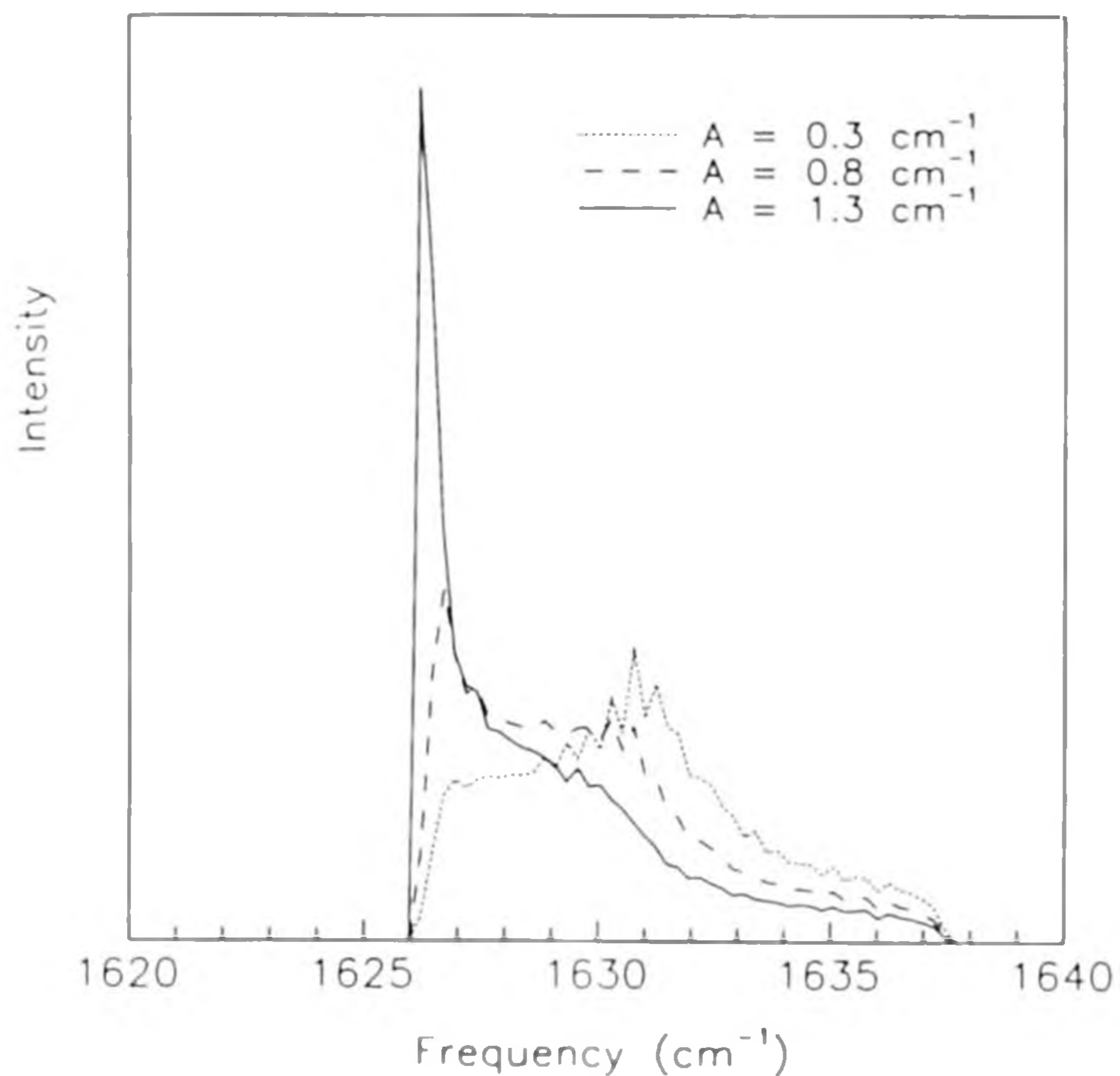


FIG. 2. Luminescence intensities calculated for different values of the anharmonicity constant A .

From the eigenvalues and eigenvectors of the two-vibron Hamiltonian, it is clear that a quasibound bivibron state is present on the lower-energy side of the spectrum, but is not split off. It is not visible in the $\mathbf{K}=0$ density of states because it is only a single state among 18 412 two-vibron states. Calculations with other anharmonicity constants A show that the $\mathbf{K}=0$ density of state is not significantly influenced by value of A .

This is different for the luminescence and Raman intensities of the two-vibron line. Because of the large uncertainty in the anharmonicity constant given by Kato *et al.*, $A=0.8\pm 0.5$ cm^{-1} , we have calculated these intensities for $A=0.3$, 0.8 , and 1.3 cm^{-1} . The lumines-

cence spectrum at $\mathbf{K}=0$ calculated from Eq. (33) has the same shape as the calculated Raman spectrum; they differ only by a constant factor. The results are plotted in Fig. 2. One observes that the line shape changes dramatically if the anharmonicity constant is changed by only 1.0 cm^{-1} . For $A=0.3$ cm^{-1} the overtone state is so strongly coupled to the two-vibron states that it is not visible in the spectrum and this spectrum resembles the $\mathbf{K}=0$ density of states. For $A=0.8$ cm^{-1} we begin to observe a quasibound state. The peak resulting from this quasibound state appears on the low-energy side of the spectrum. For $A=1.3$ cm^{-1} the quasibound state becomes much more pronounced and the spectrum consists of a sharp peak with a broad shoulder on the high-energy side. It is still quasibound, however, because it lies within the band of two-vibron states.

We can compare the shape of the calculated $\mathbf{K}=0$ luminescence and Raman-scattering spectrum with the narrow-band singlet luminescence and Raman-scattering spectra measured by Kato *et al.*¹ In the luminescence experiments the NaNO_2 crystal was excited by a laser with a photon energy of 17 cm^{-1} above the excitation energy of the singlet exciton state. In this way, besides the singlet exciton, only phonons with energies below 17 cm^{-1} can be excited. These acoustic phonons have wave vectors close to the zone center, and therefore, also, the excitons will have small $|\mathbf{K}|$. Because of the low temperature in the experiments (2 K), the redistribution of the exciton wave vectors over the Brillouin zone will be slow^{23,24} and the luminescence spectrum is generated by states with wave vectors close to zero. In Fig. 3 we have compared the $2\nu_2$ line shape measured in these experiments with the luminescence and Raman-scattering spectrum calculated

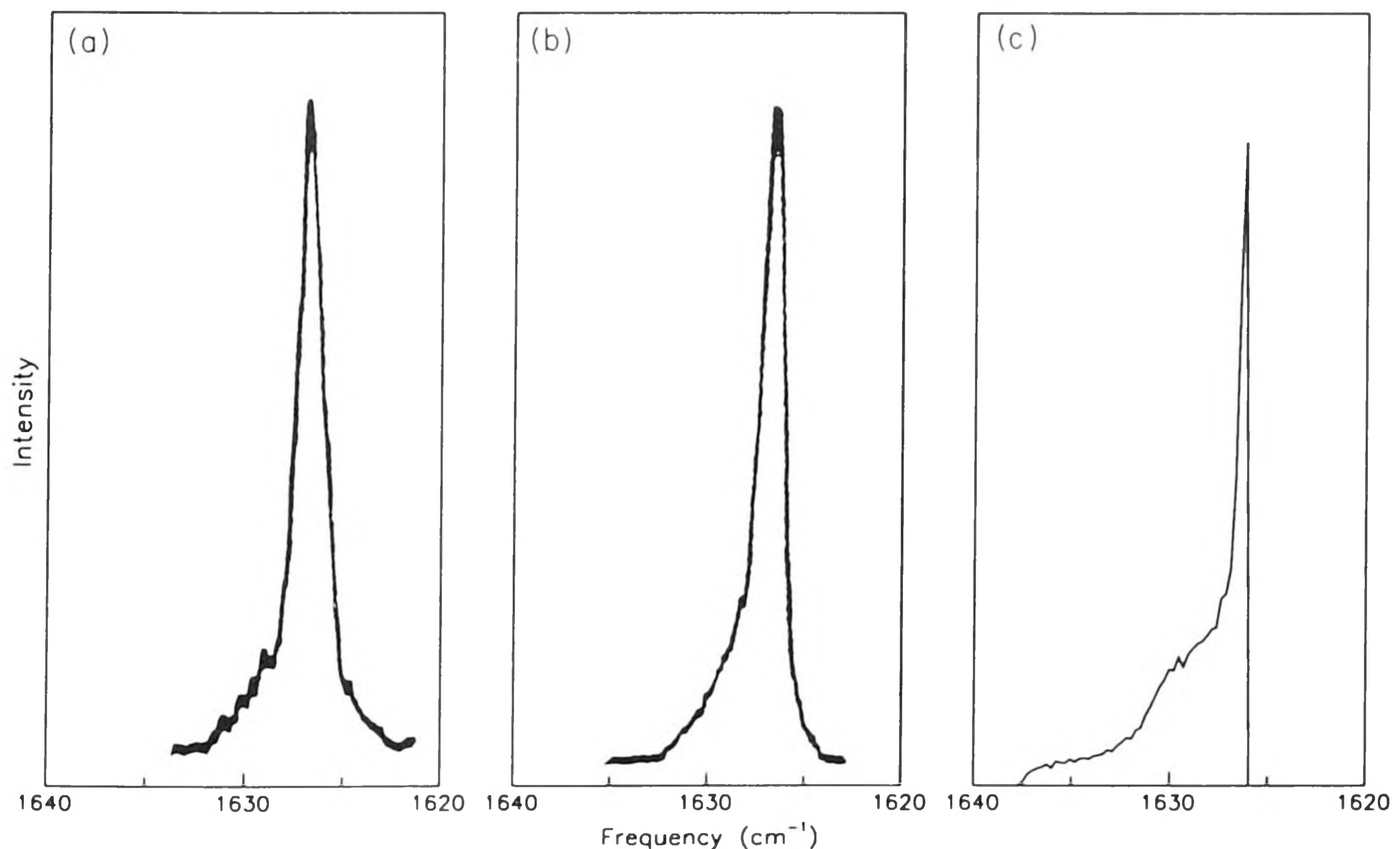


FIG. 3. Comparison between the measured Raman-scattering line (left), narrow-band singlet luminescence line (middle), and calculated Raman and luminescence lines at $\mathbf{K}=0$ (right). The energy scale is reversed, and the experimental peaks are shifted to the position of the calculated peak.

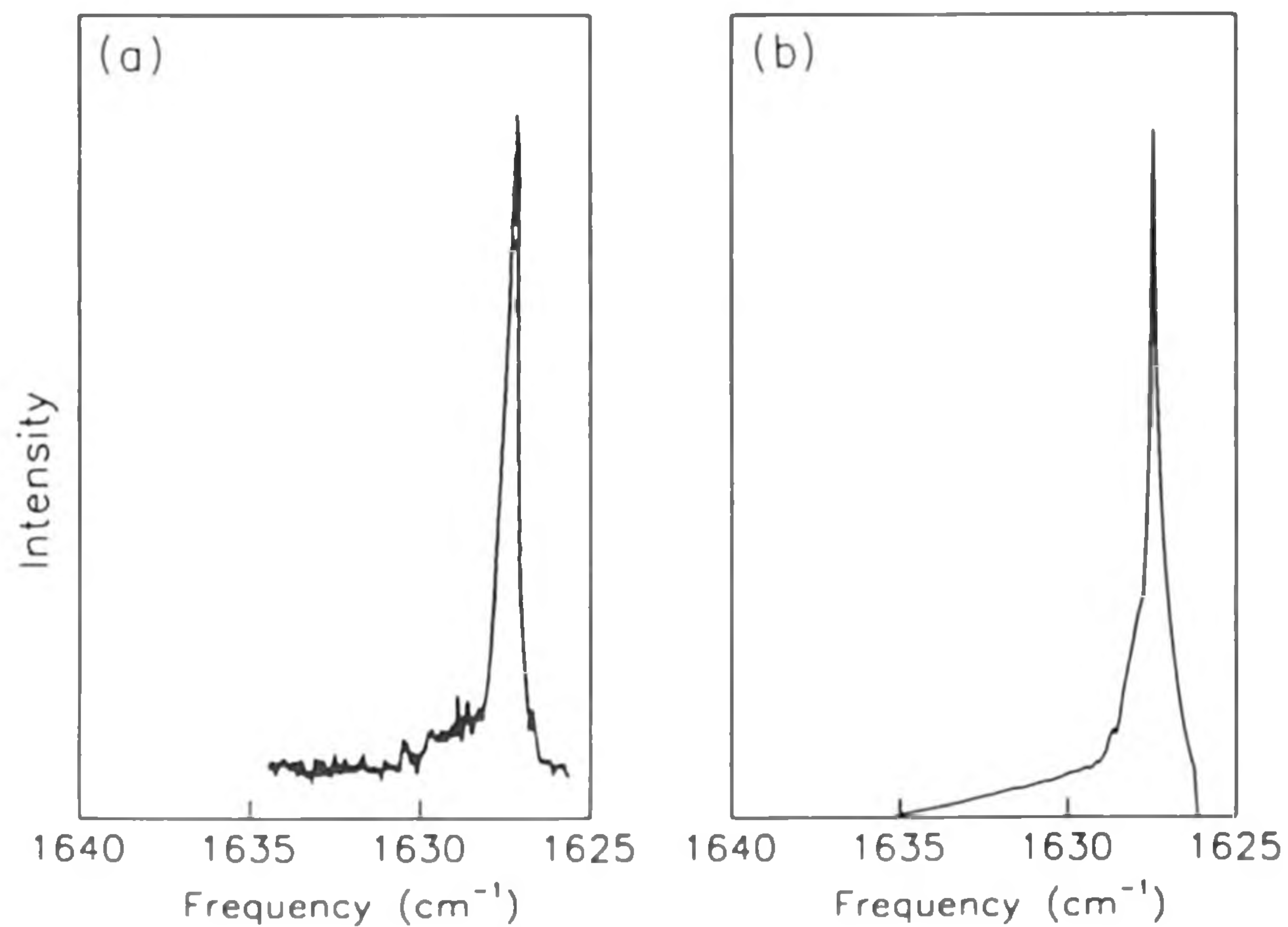


FIG. 4. Comparison between the measured (left) and calculated (right) triplet luminescence intensities.

for $A = 1.3 \text{ cm}^{-1}$, which gives the best correspondence. In order to compare the calculation with the experiments, we have reversed the energy scale.

Kato *et al.* also performed measurements on the triplet luminescence spectra of the overtones of the ν_2 vibration. The NaNO_2 crystal was excited by a mercury lamp, which leads to a broadband excitation. Beside the triplet exciton, lattice vibrations with wave vectors throughout the Brillouin zone are generated. Triplet excitons with wave vectors in the entire Brillouin zone give rise to luminescence. We have integrated the luminescence intensities over the Brillouin zone, and under the assumption that the \mathbf{K} distribution of triplet exciton states is uniform, we can compare our result with the measured $2\nu_2$ line. The correspondence between the measured and calculated lines is good, as can be seen in Fig. 4, where we have again used an anharmonicity constant $A = 1.3 \text{ cm}^{-1}$. The bivibron peak in the calculated spectrum is very narrow because the intermolecular anharmonicity $W(\mathbf{K})$ that causes the dispersion of the bivibron is very small, typically 0.005 cm^{-1} , and the coupling to the two-vibron states is weak.

Finally, we may compare the calculated luminescence intensities with the spectrum measured by broadband excitation of the singlet exciton state of the NaNO_2 crystal.²⁵ Since the dispersion of this singlet state is of the same order of magnitude as the dispersion of the two-vibron band, we have to account for the exciton dispersion. In the calculation of the luminescence spectrum of the single-vibron state in the previous paper, we have assumed a cosine-shape dispersion of the singlet exciton band and a width of 5.0 cm^{-1} . This yielded very reasonable results for the line shape of the ν_2 luminescence,¹⁴ and so we use the same model in the calculation of the line shape of the $2\nu_2$ luminescence following broadband singlet excitation. For these calculations we again used $A = 1.3 \text{ cm}^{-1}$ because in the previous calculations this gave a good correspondence with the experimental results. In Fig. 5 we have compared the calculated line shape of the broadband singlet luminescence peak with the measured one. We observe that the width of the mea-

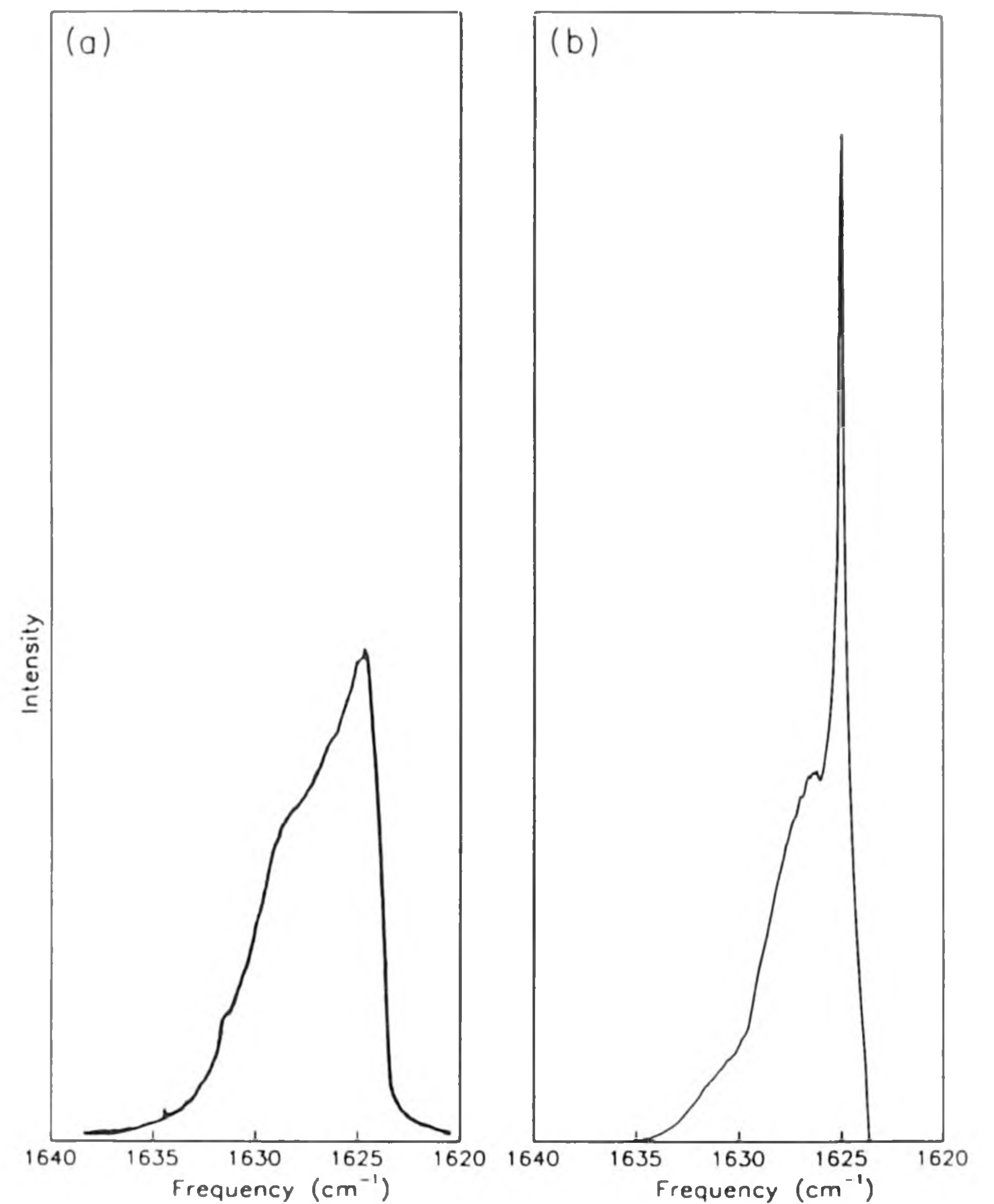


FIG. 5. Comparison between the measured (left) and calculated (right) broadband excited singlet luminescence intensities. The calculations were performed with $A = 1.3 \text{ cm}^{-1}$.

sured band is about 3 cm^{-1} larger than the calculated width. In the calculations in the previous paper¹⁴ on the singlet luminescence peak of the ν_2 vibration, it was shown that the width of the calculated band was also about 3 cm^{-1} too small. This leads to the conclusion that the assumed width of the singlet exciton band is probably slightly underestimated. The calculated band has a sharper peak at the lower-energy side originating from the quasibound states. In the measured band this peak is not so pronounced. The $2\nu_2$ band was measured at $T = 4.2 \text{ K}$. It was demonstrated that at such low temperatures the singlet states are not uniformly distributed throughout the Brillouin zone^{23,24} and the measured line shape might be distorted because of this nonuniform distribution.

In conclusion, we can say that the coupling between the nitrite overtone vibration and the two-vibron states in solid NaNO_2 is weak enough to allow for a quasibound bivibron to be formed, as was already concluded from the luminescence experiments by Kato *et al.*¹ If we assume an anharmonicity constant of 1.3 cm^{-1} for the ν_2 bending vibration of the nitrite ion, which is somewhat higher than the value of $0.8 \pm 0.5 \text{ cm}^{-1}$ estimated by Kato *et al.*, we can very well explain the luminescence line shapes measured by narrow-band excitation of the singlet exciton state and by broadband excitation of the triplet exciton state, as well as the Raman line shapes. Also the calculated luminescence line shape for broadband excitation of the singlet exciton state is in reasonable agreement

with the measured line shape, if we assume a cosine-shaped dispersion for the singlet exciton band and a width of somewhat more than 5 cm^{-1} for this band.

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