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Anharmonicity and Fermi resonance in the vibrational spectra of a CO₂ molecule and CO₂ molecular crystal: Similarity and distinctions

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Abstract

The vibrational spectra of a molecule and related molecular crystal are systematically analyzed theoretically with the account of the influence of anharmonic interactions between the vibrations. The specific anharmonism-induced features in the spectra of a molecule and crystal are revealed, and spectral lineshapes at varied strength of anharmonic interaction are simulated. The proposed general theoretical approach is used for fitting the experimental vibrational spectra of CO₂ substance in gas and molecular crystal phases. Pretty good coincidence of experimental data with theoretical results is demonstrated, and the constants of anharmonic interaction are obtained. The proposed theoretical approach can be used to interpret the bands in the Raman and infrared absorption spectra of various complex molecules and crystals.

KEYWORDS

anharmonism, CO₂ molecule, Fermi resonance, molecular crystal, vibrational spectra

1 | INTRODUCTION

Vibrational spectra obtained either by infrared absorption (IR) or Raman scattering (RS) methods are an important source of information about the inner structure of molecules and solids. The analysis of the spectral positions of vibrational features, their intensities, and line shapes provides deep insight into the structure of molecular oscillators (or phonons in solids), nature of interactions, and strength of bonding. In many cases, the analysis of vibrational spectra in the harmonic approximation gives excellent results. However, there are many cases when the description within this approximation fails. The source of the deviations from the harmonic behavior is the coupling of different oscillators within the same molecule or crystal due to the anharmonicity of their potential energy function.

Interactions between different oscillators in a molecule or crystal lead to significant shifts of the

spectral positions of the vibrational bands from the ones predicted by simple models that are based on the harmonic oscillators. Moreover, the anharmonicity can cause the emergence of apparent “extra” bands. First experimental observations of such spectral features were reported for simple molecules CO₂,^[1,2] H₂O,^[3] HCN, and DCN^[4] in gas state as well as for more complex species CCl₄,^[5] C₆H₅Cl^[6], and so forth. The understanding of these experimental results was achieved based on the accounting of the anharmonicity of different orders in the series expansion of the potential. In this case, the potential energy of a molecule is no more presented by a quadratic function of the displacements of atoms from their equilibrium positions in the molecule. The nonharmonic potential dependence is written as a power series in the displacements of atoms from equilibrium positions. In accordance with the order in the expansion, the corresponding terms can be

considered as nonharmonic terms of the third order, fourth order, and so forth.

The best studied case of anharmonicity-related spectral features is the one caused by the third-order term in the expansion of the potential energy. It was first theoretically interpreted by Fermi^[7] as the result of the interaction of a fundamental vibration with an overtone. This case is known as Fermi resonance (FR). This type of resonance is frequently observed and investigated in the spectra of molecules.^[1–7]

The approach proposed by Fermi^[7] is widely used by many authors for the explanation of different anharmonicity-induced vibrational features in the spectra. It permits, in particular, to determine the unperturbed fundamental band position that is shifted due to FR if the ratio of integral intensities of Fermi doublet (the bands that arise in Raman spectra, from the interaction of a fundamental band and an overtone of some low frequency band) is known. However, if the components of Fermi doublet (Fermi diad) are strongly overlapped, the quantitative analysis of the unperturbed bands intensities ratio as well as determination of the anharmonicity constants is not always possible in the framework of the approach proposed by Fermi.^[7]

FR in solids was studied using the traditional Raman scattering on phonons^[8–10] and phonon-polaritons.^[11–13] Nonlinear features of both components of Fermi doublet in the spectra of molecular crystals were studied in the paper.^[14] It should be noted that in molecular crystals, the vibrations of atoms in a molecule are no more independent; due to the interactions between the molecules, they acquire a collective character and appear as phonons that are characterized both by frequency and wave vector. Despite the fact that FR has been explained in 1931,^[7] the efficiency of different theoretical models for describing vibrational spectra of molecular crystals is still under discussion.^[15–17]

In the present paper, we analyze the difference between the influence of anharmonism on the spectra of a molecule and a molecular crystal built of the same molecules. We propose the approach to obtain the values of anharmonic interaction parameters directly from the experimental data. The procedure is based on the detailed fitting of the experimental line shapes (either in IR or RS spectra) and obtaining the constants, which characterize the anharmonicity, from the comparison of the best fit with the experimental spectra. The formula that is used for fitting is obtained for the simplest case accounting for the interaction of two oscillators with the frequencies that differ by, approximately, two times, namely, the interaction of the fundamental vibration of a high frequency oscillator with the first overtone of another low frequency oscillator.

The approach advanced was applied for the analysis of anharmonism-related features in the spectra of CO₂ gas and CO₂ molecular crystal. This molecule is, on the one hand, rather simple, and, on the other hand, it is very important in various areas of human activities. Therefore, the properties of CO₂ are extensively studied both in gas and solid states as well as in solutions. At present, the studies are conducted in the fields of biology,^[18] geology,^[19,20] ecology,^[21] energetics,^[22,23] sensorics,^[24,25] combustion processes,^[26] food industry,^[27] and so forth. We have measured Raman spectra of the same substance (CO₂) in gas and crystal phases and compared with the theoretically predicted spectra.

2 | ANHARMONICITY PARAMETERS DETERMINATION FOR MOLECULES

We analyze the vibrations of a separate molecule that is not subjected to any external influence. The interaction between different vibrations of this molecule is caused by the anharmonicity of its potential energy. The mutual influence of the vibrations is supposed to be weak; therefore, the perturbation theory approach can be used. The Hamiltonian of a molecule can be written as a sum of two terms: the operator describing the non-interacting vibrational states (oscillators) H_0 and the operator that is responsible for an interaction between them, V :

$$H = H_0 + V. \quad (1)$$

Here, it is convenient to present V as a series in powers of normal coordinates, Q_α ,

$$V = \frac{1}{3!} \sum_{\nu, \mu, \lambda} V^{\nu, \mu, \lambda} Q_\nu Q_\mu Q_\lambda + \frac{1}{4!} \sum_{\nu, \mu, \lambda, \eta} V^{\nu, \mu, \lambda, \eta} Q_\nu Q_\mu Q_\lambda Q_\eta + \dots, \quad (2)$$

where indexes ν, μ, λ, η enumerate the molecular vibrations.

The wave function of the molecule is presented by a linear combination of the eigenfunctions of non-interacting oscillators, ϕ_n .

In the present study, we analyze the vibrational states, φ_1 and φ_2 , with close energies $E_1 \approx E_2$ but with different origins of the interacting states: The state φ_1 corresponds to a fundamental vibration with $E_1 = \Omega_C$, whereas φ_2 corresponds to an overtone vibration $E_2 = 2\Omega_B$. The condition of quasidegeneration of these modes energies is crucial for the observation of Fermi-resonance shapes in the spectra. The Schrodinger equation with the Hamiltonian (Equation 1) was considered, for example, in the book^[13] using the unperturbed wave function of a

molecule in the form:

$$\phi = \alpha\phi_1 + \beta\phi_2, \quad (3)$$

where α and β are constants.

The energies and wave functions of the interacting oscillators are the following:

$$E_{\pm} = \frac{\bar{E}_1 + \bar{E}_2}{2} \pm \frac{\kappa}{2} = E_{av} \pm \frac{\kappa}{2}, \quad (4)$$

$$\phi_+ = \sqrt{\frac{\kappa + \delta}{2\kappa}}\phi_1 + \sqrt{\frac{\kappa - \delta}{2\kappa}}\phi_2, \quad (5a)$$

$$\phi_- = \sqrt{\frac{\kappa - \delta}{2\kappa}}\phi_1 - \sqrt{\frac{\kappa + \delta}{2\kappa}}\phi_2, \quad (5b)$$

where κ and δ are described by the following expressions:

$$\kappa = \sqrt{\delta^2 + 4|V_{12}|^2}, \quad (6)$$

$$\begin{aligned} \delta &= \bar{E}_1 - \bar{E}_2 = E_1 - E_2 + (V_{11} - V_{22}) \\ &= \delta_0 + (V_{11} - V_{22}), \end{aligned} \quad (7)$$

$V_{ij} = \langle i|V|j \rangle$ is the matrix element of the perturbation operator in Equation 1 between the functions ϕ_i, ϕ_j in Equation 3; that is, the corrections V_{11} and V_{22} to the energy are caused by the anharmonic term in the series expansion of the potential energy of the molecule. $\delta_0 = E_1 - E_2 = \Omega_C - 2\Omega_B$ is called the natural difference; it is the difference between the energies of two non-interacting oscillators.

The value $(V_{11} - V_{22})$ in Equation 7 describes the spectral shift of both vibrational states that is caused by interaction: the larger interaction, the more significant changes in energy.

Besides, the interaction between the oscillators, that is, described by the operator V , causes the change of the intensities of the corresponding spectral bands, which leads to significant transformations of the spectrum.

The relations describing the integral intensities of Fermi doublet components were given in the paper by Hanson^[1] for Raman scattering, and later, they were described in details in the book^[13] for infrared absorption. In both works, it was noted that dipole moment d_C (or tensor polarizability α_{ii}) of the fundamental transition is much larger than the one of the overtone d_{BB} . Therefore, the contribution of d_{BB} or α_{ii} can be omitted when one analyzes the integral intensities of Fermi doublet bands (I_+, I_-). The expressions for the integral intensities of the doublet bands in the absorption spectrum are

$$I_+ = \frac{\kappa + \delta_0}{2\kappa} I_C, I_- = \frac{\kappa - \delta_0}{2\kappa} I_C, I_C \sim d_C^2. \quad (8)$$

It is seen from Equations 6–8 that, if $\delta_0 = \Omega_C - 2\Omega_B \ll \kappa$, two bands of close intensities $I_+ \approx I_- \approx (I_C)/2$ should be observed in the spectrum instead of an intense fundamental one.

The Equations 4 and 8 give the positions and integral intensities of the bands in the Fermi doublet. However, for comprehensive theoretical description of the FR phenomenon, one has to calculate in detail the spectral distribution of the intensity for certain objects (molecules or solids) and to compare it with the corresponding experimental spectra.

The method for the detailed calculation of the line shapes of the vibrational bands under the FR condition has been proposed in Ratajczak and Yaremko.^[28] Note that in Ratajczak and Yaremko^[28] the analysis of anharmonic effects has been done for the case of crystals. This approach can be modified to obtain the spectral shapes of the molecular vibrations. In the following section of this work, we will simplify the expressions obtained in Ratajczak and Yaremko^[28] by excluding interactions of intramolecular vibration with lattice phonons and interactions between the molecules in the crystal.

3 | SIMULATION OF ABSORPTION SPECTRA FOR A MOLECULE AND THE EFFECT OF THE THIRD-ORDER ANHARMONICITY

In the present section, we analyze the spectral shapes of the Fermi doublet components of a molecule. Here, we will restrict the expansion to the third-order term only. The anharmonicity term of third order Equation 1 for a molecule under the condition of FR can be written as follows:

$$V^{(3)} = \frac{1}{2} V^{BBC} Q_B^2 Q_C = \Gamma Q_B^2 Q_C, \quad (9)$$

where Γ is the anharmonicity parameter.

Taking into account that normal coordinate operator changes the oscillator wave functions, ϕ_{n_ν} , as follows:

$$Q_\nu \phi_{n_\nu}(Q_\nu) = \sqrt{\frac{n_\nu}{2}} \phi_{n_\nu-1}(Q_\nu) + \sqrt{\frac{n_\nu+1}{2}} \phi_{n_\nu+1}(Q_\nu), \quad (10)$$

where n_ν are the average numbers of phonons, $\nu = B, C$, one can show that matrix elements of the operator $V_{i,j}^{(3)} = \langle i|V^{(3)}|j \rangle$ (see Equation 9) satisfy the following relations: $V_{C,C}^{(3)} = V_{BB,BB}^{(3)} = 0$, and $V_{C,BB}^{(3)} \neq 0$. Therefore, the matrix element $V_{C,BB}^{(3)} \neq 0$ causes the intermixing of

vibrational states and redistribution of the intensities between the components of Fermi doublet^[13] as it is shown in Figure 1.

Figure 1 shows the typical theoretical dependences describing the positions of the bands and their intensities at different values of the constant Γ . The Curve 1 describes the vibrational spectrum of a molecule in the case of non-interacting oscillators ($\Gamma = 0$). The spectrum is dominated by a fundamental vibrational band, whereas the overtone of another low energy oscillator is not seen due to its extremely low intensity. In the theoretical spectrum, the overtone is placed at the coordinate origin; thus, the fundamental vibration is shifted with respect to the overtone by the space δ_0 (the natural difference). Curves 2–5 illustrate the anharmonicity-induced changes of the spectrum: with increasing constant Γ , an “extra” weak band appears at the overtone energy. The intensity of this peak increases with Γ , whereas the intensity of the fundamental vibration is diminished, and the space between the components of the doublet becomes larger. At $\Gamma = 0.4$, the intensities of two bands become almost equal. Thus, this Figure 1 demonstrates that the overtone gains intensity at the cost of the fundamental band.

Figure 2 demonstrates the influence of another parameter, the natural difference, δ_0 , on the spectra: with increasing of the initial space δ_0 between the states, the intensity of the overtone is diminished at the unvaried Γ value. The above figures illustrate that one can estimate the parameters responsible for the character of a spectrum by comparing the theoretical and experimental spectra. In what follows, we will demonstrate how to apply these results for the analysis of experimental data for CO₂ molecule.

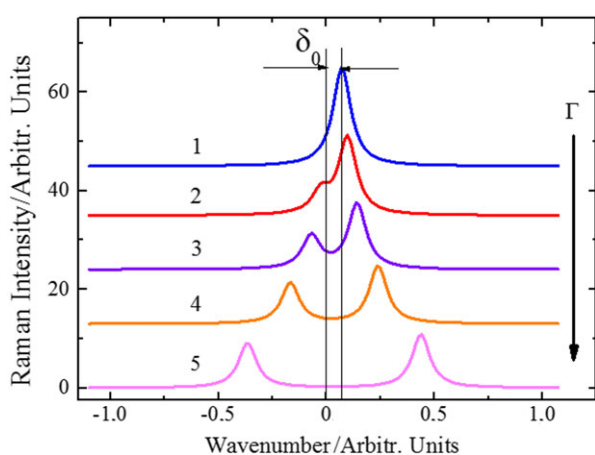


FIGURE 1 Influence of the interaction between intramolecular states on the spectral positions and intensities of a fundamental vibration and an overtone. The values of the parameter Γ , which characterizes the interaction, are: Curve 1, $\Gamma = 0.001$; Curve 2, $\Gamma = 0.05$; Curve 3, $\Gamma = 0.1$; Curve 4, $\Gamma = 0.2$; and Curve 5, $\Gamma = 0.4$ [Colour figure can be viewed at wileyonlinelibrary.com]

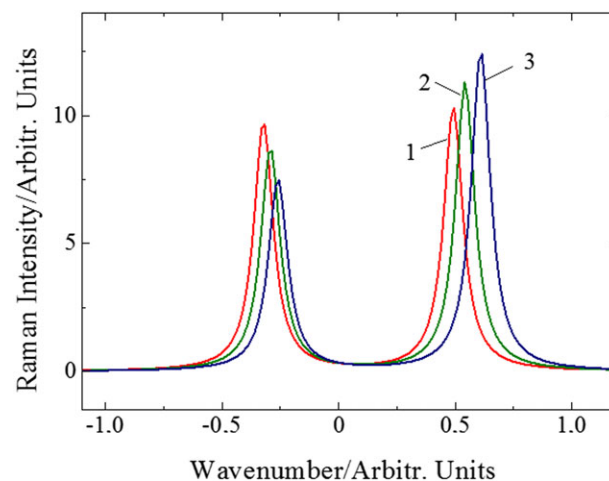


FIGURE 2 Change of the bands positions and their intensities as a function of the constant δ_0 (the initial space between the bands involved in Fermi resonance) at interaction constant $\Gamma = 0.4$: Curve 1, $\delta_0 = 0.07$; Curve 2 vibrational $\delta_0 = 0.15$; and Curve 3, $\delta_0 = 0.25$ [Colour figure can be viewed at wileyonlinelibrary.com]

4 | COMPARISON OF THE THEORETICAL RESULTS WITH THE EXPERIMENTAL DATA ON CO₂ MOLECULE

As noted earlier, experimental investigation of vibrational spectra and FR effects in gases and in liquid solutions had been done for many molecules (see Hanson, Langseth, Darling and Dennison, Douglas and Sharma, Lisitsa and Malinko, Plyler et al., and Dennison^[1–6,29] and numerous references in Lisitsa and Yaremko^[13]). Here, we will consider only the case of FR in CO₂ molecule, which is the most discussed one in literature. CO₂ is a linear center-symmetrical molecule; its symmetry is described by the point symmetry group, $D_{\infty h}$. The molecule has three internal vibrations: fully symmetrical vibration Σ_g^+ , labeled as ν_1 ; asymmetrical bending, π_u , labeled as ν_2 , and stretching vibration Σ_u^+ , labeled as ν_3 . The values for ν_2 and ν_3 were obtained in harmonic approximation in Lisitsa and Yaremko and Dennison,^[13,29] and they are $\nu_2 = 667 \text{ cm}^{-1}$ and $\nu_3 = 2349 \text{ cm}^{-1}$. The value of ν_1 cannot be obtained in harmonic approximation because this fully symmetrical vibration takes part in the interaction with the overtone $2\nu_2$ of the asymmetrical bending vibration ν_2 ($2\nu_2 = 1334 \text{ cm}^{-1}$). Such interaction is possible because, according to the group theory, the character of the reducible representation of the overtone $2\nu_2$ is a sum of two characters of the following irreducible representations: $\{\chi(\pi_u)\}^2 = \Sigma_g^+ + \Delta_g$.

In Raman spectra, only the fully symmetrical vibration ν_1 should be observed, whereas ν_2 and ν_3 should be

seen in IR spectra. The overtone $2\nu_2$ (as it was noted above) is too weak to be observed. However, due to interaction of ν_1 and $2\nu_2$ vibrations, two strong bands (Fermi doublet) are observed in Raman spectra. Indeed, the experimental results demonstrate the doublet of strong bands $\nu' = 1389 \text{ cm}^{-1}$ and $\nu'' = 1286 \text{ cm}^{-1}$ with the intensity ratio $\approx 1/0.59$.^[1] The difference between the energies of this doublet and the average energy ν_{av} (up to a factor h) is, respectively, $\nu' - \nu'' = 103 \text{ cm}^{-1}$, $\nu_{av} = (\nu' + \nu'')/2 = 1337.5 \text{ cm}^{-1}$. Fermi doublet (ν' and ν'') formation for two different cases ($2\nu_2 < \nu_1$ and $\nu_2 > \nu_1$) is schematically shown in Figure 3. Using the experimental data (ν' and ν''), one can solve a reciprocal problem and find the energy of the unperturbed fully symmetrical vibration, ν_1^{up} . In the case of CO_2 molecule, the difference between the unperturbed components of the doublet calculated using the above experimental data is $2(\nu_{av} - 2\nu_2) = \delta_0 \approx 7 \text{ cm}^{-1}$. Correspondingly, the fundamental band must be located at $\nu_1^{up} = \delta_0/2 + \nu_2 \approx 3.5 \text{ cm}^{-1} + 1337.5 \text{ cm}^{-1} = 1341 \text{ cm}^{-1}$. Here, we did not account for the possible variation of δ due to anharmonism of higher orders (Equation 7), and so, in this approximation, δ_0 and δ coincide. (However, it should be noted that non-zero matrix elements $V_{C,C^{(4)}} \neq 0$, $V_{BB,BB^{(4)}} \neq 0$ lead to the additional shift of the vibrations energies).

One can estimate the nonharmonic interaction constant using the Equations 4 and 6:

$$\begin{aligned} \nu' - \nu'' &= \kappa = \sqrt{\delta_0^2 + 4\Gamma^2}, \Gamma^2 = \frac{1}{4}(\kappa^2 - \delta_0^2) \\ &= 2630 \text{ cm}^{-2}, \Gamma \approx 51 \text{ cm}^{-1}. \end{aligned}$$

These values of the parameters were obtained in the simplified approach that allows only the analysis of the integral intensities. Application of such approach for the description of experimentally observed lineshapes gives unsatisfactory results. It is necessary to use the method like the one proposed in Ratajczak and Yaremko.^[28]

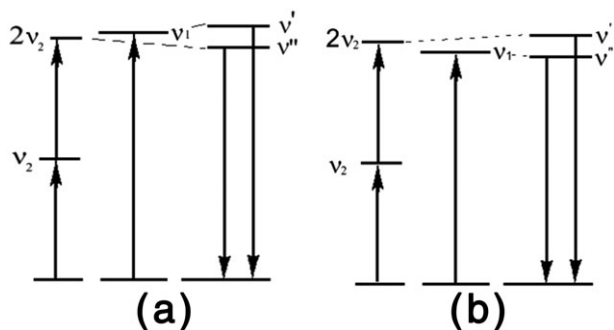


FIGURE 3 Schematic diagram of vibrational energy levels of CO_2 molecule and Raman bands origin for the cases: (a) $2\nu_2 < \nu_1$ and (b) $2\nu_2 > \nu_1$

Application of this method gives the spectral dependences shown in Figures 1 and 2.

To optimize the fitting of experimental spectra, we have varied the parameters and obtained pretty well agreement of theoretical and our experimental curves. Figure 4 shows the comparison of the doublet of strong bands experimentally observed for the gaseous phase of CO_2 with the calculated ones. Raman spectra were measured using Raman spectrometer DFS-52 and solid state laser ($\lambda = 457 \text{ nm}$) for excitation.

Using the experimentally observed ratio of doublet bands intensities $1/0.65$ and the calculated constant Γ , we have simulated Fermi doublet components in the same way as it was done in the previous section for Figures 1 and 2. The results are shown in Figure 4. Correlation of the Curves 1 and 2 is pretty good, which demonstrates the applicability of the proposed approach. The fitting parameters are the following: $\Gamma = 0.48$ and $\delta_0 = 0.31$. The latter value differs from the one obtained before ($\delta_0 \approx 7 \text{ cm}^{-1}$); this can be caused by the anharmonicity of higher orders in Equation 7 (e.g., of the fourth order that was neglected in previous calculations). The higher order terms in the series expansion can lead to the renormalization of harmonic energies, and, consequently, to the change of δ_0 .

In the present section, FR was analyzed with the account of the third-order anharmonism. However, the fourth-order anharmonism can also play an important role in the description of molecular vibrations. It causes the shift of main vibration energies, and these anharmonic corrections are energy-dependent (i.e., the corrections to a certain energy depend on this energy value). Therefore, the energies of the fundamental band and overtones would change differently when the fourth-order terms are taken into account. As a result,

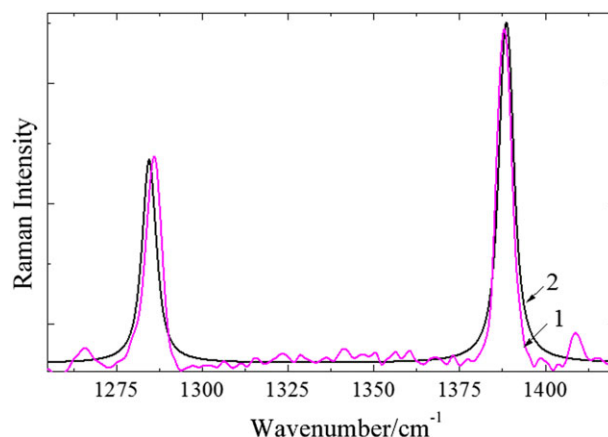


FIGURE 4 Comparison of the experimental spectrum of Fermi doublet bands of CO_2 gas (Curve 1) with the simulated spectrum of CO_2 molecule (Curve 2) [Colour figure can be viewed at wileyonlinelibrary.com]

the value δ would be changed (as it follows from Equation 7). Comparison of the experimental and fitted curves shows that, indeed, experimentally obtained δ_0 is not equal to the one obtained in the third-order approximation. The influence of the fourth-order anharmonicity will be explicitly considered below when FR in crystals will be analyzed.

5 | FERMI RESONANCE IN THE CARBON DIOXIDE MOLECULAR CRYSTAL

The FR features in crystals are more complicated than in molecules. The crucial difference is that anharmonic interactions take place between the phonons, which are dependent on wave vector. Thus, in the analysis of optical transitions, both energy and momentum preservation laws should be accounted for. Dispersion of phonon branches leads to diversification of the possibilities for a fundamental phonon to interact with overtone phonons (in other words, with the phonons from the wide band of two-phonon states (TPS)). As it will be shown below, anharmonic interaction with phonons leads to additional, as compared with a molecule, variation of the intensities and positions of the vibrational bands and strongly distorts their line shapes.

Here, we analyze the molecular crystal of carbon dioxide and compare its vibrational spectra with the ones of CO₂ molecule. The lattice of CO₂ molecular crystal is characterized by $P4_2/mnm$ (D_{4h}^{14}) space group with two molecules ($z = 2$) per elementary cell.^[30] The factor (point) group of the crystal is D_{4h} , which is a subgroup of $D_{\infty h}$. Therefore, correlation between the symmetries of the vibrations for both groups is rather simple, which is clearly seen from the Table 1. By applying the group theory approach, one can show, similarly to the case considered for CO₂ molecule, that the reducible representation of the overtone $2\nu_2$ in the crystal CO₂ is the sum of the following irreducible representations: $\{\chi(E_u)\}^2 = A_{1g} + B_{1g} + B_{2g}$. This result means that, due to anharmonicity, in CO₂ crystal, the overtone $2\nu_2$ can interact with the fundamental vibration ν_1 of A_{1g} symmetry.

The principal relations describing intensity distributions in IR and RS spectra were obtained in Lisitsa and

Yaremko, Ratajczak et al., and Yaremko et al.^[13,32,33] In these papers, the analysis has been done including the anharmonism of the fourth order. It means that all terms in Equation 2 have been taken into a consideration.

In the case when TPS are involved in the anharmonic interaction, one has to account for the pairs of phonons with the energies $\omega(k-q)$ and $\omega(q)$; here k is the wave vector of the exciting photon, that is, FR takes place between the fundamental phonon (at $k \approx 0$) and TPS belonging to the broad band (the width of TPS band is determined by the dispersion of the corresponding phonons). General expression describing RS intensity at FR in the crystal is written as follows^[33]:

$$I(\omega) \sim [1 + n(\omega)] \chi_c^2 \frac{2f_2 a^2 + R_2^c b^2}{c^2 + d^2}, \quad (11)$$

χ_c and R_2^c are the scattering tensor per unit cell and damping constant for the fundamental band Ω_c , respectively. The value $n(\omega)$ is the average number of photons. Values a, b, c, d are the factors that depend on the crystal parameters such as anharmonic constants of the third and fourth orders (Γ, A^P ,^[32,33] respectively), as well as on temperature and complex function $f(\omega)$, which describes the density of TPS:

$$f(\omega) = f_1 + if_2 = \frac{1}{N} \sum_q \frac{1 + 2n_q^p}{\omega - 2\omega_{q,p} + i\gamma_p}, \quad (12)$$

$$\omega_{q,p} = \omega_{0,p} + \sum_{l=1}^L \left[M_{l,x}^p \cos(lq_x a_x) + M_{l,y}^p \cos(lq_y a_y) + M_{l,z}^p \cos(lq_z a_z) \right], \quad (13)$$

here, n_q^p and $\omega_{q,p}$ are the average number of phonons and their energies, respectively. $M_{l,x}^p, M_{l,y}^p, M_{l,z}^p$ are the coefficients that characterize dispersion of the phonon branches.

Value γ_p is the damping constant of the overtone “ p ”; damping arises owing to the interaction of “ c ” and “ p ” vibrations with other vibrations of the lattice; phonon energies $\omega_{q,p}$ are presented by a series of harmonics in q -space, (for more details see Ratajczak et al. and Yaremko et al.^[32,33]).

In theoretical calculations, it is convenient to use the parameter, $\delta_0 = \omega_c - 2\omega_p$ similarly to the case of a molecule, which describes the difference between the unperturbed states involved in FR.

An important factor for understanding FR spectrum in crystals is the ratio between anharmonic constants, Γ and A^P . This is clearly demonstrated by the dependencies

TABLE 1 Symmetry of vibrations in CO₂ molecule and CO₂ crystal^[31]

Freq.	Mol. CO ₂ symm. $D_{\infty h}$	Cryst. CO ₂ symm. D_{4h}
ν_1	$\Sigma_g^+ \rightarrow$	A_{1g}
ν_3	$\Sigma_u^+ \rightarrow$	A_{2u}
ν_2	$\pi_u \rightarrow$	E_u

obtained using Equations 11–13 and shown in Figures 5 and 6.

At first, we analyze the influence of each anharmonicity constant separately. Figure 5 demonstrates the influence of the constant A^p on the lineshape of the vibrational spectra in the TPS region at $\Gamma=0$. (For simplicity, one-dimensional case $M_1^p \gg M_2^p, M_3^p$ is considered). The fundamental vibration band is not shown in

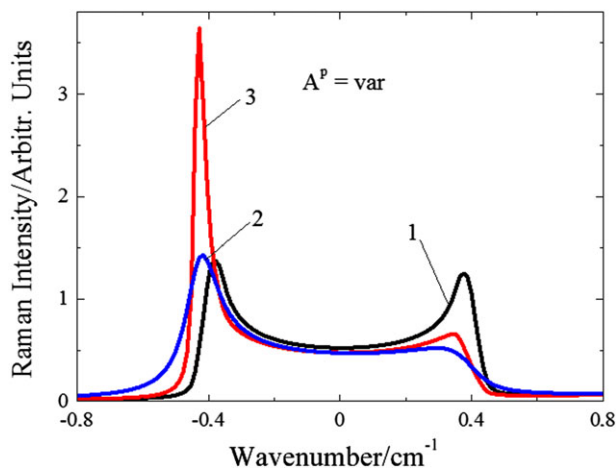


FIGURE 5 Intensity of light scattering in the region of two-phonon states at different anharmonic constant A^p values and $\Gamma = 0$. Curve 1: $A^p = -0.005$, $\gamma_p = 0.05$; Curve 2: $A^p = -0.01$, $\gamma_p = 0.05$; and Curve 3: $A^p = -0.01$, $\gamma_p = 0.01$ [Colour figure can be viewed at wileyonlinelibrary.com]

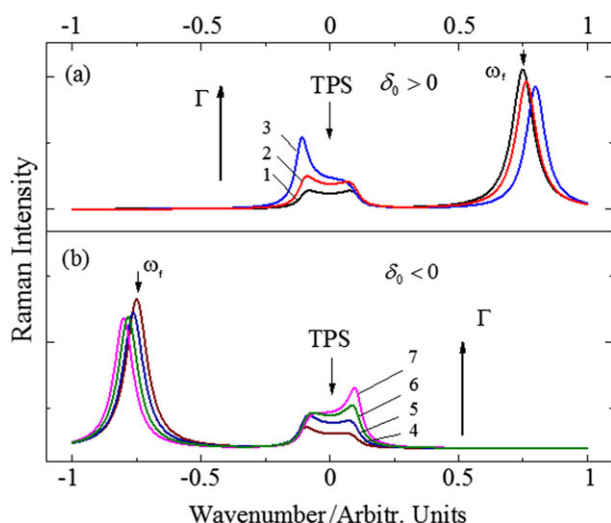


FIGURE 6 Effect of the constant Γ , that is responsible for Fermi resonance, on Raman spectra in the spectral region of two-phonon states (TPS) for different values of δ_0 : (a) $\delta_0 = 0.75$, $\gamma_p = 0.05$, $A^p = 0$: Curve 1: $\Gamma = 0$; Curve 2: $\Gamma = 0.04$; and Curve 3: $\Gamma = 0.08$; (b) $\delta_0 = -0.75$, $\gamma_p = 0.05$, $A^p = -0.005$: Curve 4: $\Gamma = 0$; Curve 5: $\Gamma = 0.006$; Curve 6: $\Gamma = 0.01$; and Curve 7: $\Gamma = 0.015$ [Colour figure can be viewed at wileyonlinelibrary.com]

this figure because it does not influence the shape of TPS band at $\Gamma=0$. The anharmonicity constant of the fourth order is negative $A^p \leq 0$ ^[21]; therefore, TPS shifts to the low energy range, and the broad band of TPS is deformed in accordance with Equation 11. When the value A^p is small, the two-phonon band is rather wide and has two maxima of almost equal intensities on both sides (Curve 1), which reflects the density of states distribution within this two-phonon band at one-dimensional dispersion law. With increasing A^p (Curve 2), the high-energy maximum diminishes whereas the low-energy maximum increases (the latter maximum is known as biphonon^[34]). The same figure demonstrates the influence of the damping constant value γ_p on the line shape (compare the Curves 2 and 3). As is seen from Curve 3, this low-frequency maximum becomes even more pronounced at low damping.

If FR is taken into consideration, that is, $\Gamma \neq 0$, the spectrum is changed. In this case, the character of the spectrum depends on the mutual arrangement of the fundamental and combination tone. Two cases that correspond to different values of the parameter ($\delta_0 > 0$ and $\delta_0 < 0$) are shown in Figure 6a,b.

Figure 6a corresponds to $\delta_0 = 0.75$. To elucidate the effect of the parameter Γ alone, we suppose that $A^p = 0$ (Figure 6a). With increasing Γ , the sharp maximum appears on the low-energy side of TPS (Curves 2 and 3), and the fundamental band ω_c is shifted to the opposite to the TPS side. It is seen that in this case ($\delta_0 > 0$), the tendency of changes in TPS spectrum is similar to the one shown in Figure 5. Thus, in the case $\delta_0 > 0$, the parameters A^p and Γ affect the spectrum identically.

Figure 6b (Curves 4–7) shows the spectral shapes corresponding to the case $\delta_0 < 0$. Here, we choose $A^p \neq 0$. It is seen that the increase of the parameter Γ (at fixed A^p) leads to the changes of the spectra that are opposite to the ones shown in Figure 6a. The Curve 4 corresponds to the parameters $A^p = -0.005$ and $\Gamma = 0$; the small maximum is seen on the low-energy side of TPS. With the increase of the parameter Γ , this maximum gradually disappears, and a new peak on the high-energy side of TPS arises (Curves 5–7, Figure 6b).

Note that in Figure 6a,b, we considered, as an example, the case of weak FR, when the natural difference between the fundamental and combination tone is sufficiently large, $\Gamma < \delta_0$; therefore, both bands are clearly observed and weakly change with increasing of Γ . However, in the realistic case of CO_2 crystal, the situation is different: Anharmonic interaction is rather strong $\Gamma > \delta_0$, and thus, very strong FR occurs. This strong interaction causes significant changes of TPS band that is clearly seen in the experimental spectra shown in Figure 7 and calculated spectra shown in Figure 8.

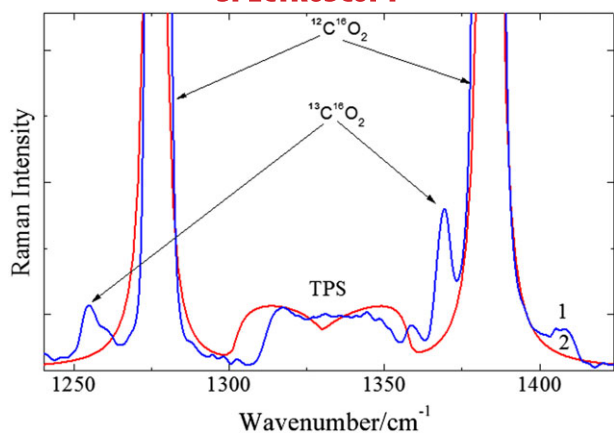


FIGURE 7 Raman spectra of CO₂ crystal: Curve 1—the experimental spectrum; Curve 2—the fitted spectrum. Fitting parameters: $\Gamma = 0.33$, $\delta_0 = 0.19$, $A^p = 0.01$, $M_{1x} = M_{1y} = 0.075$, $M_{1z} = 0.001$. TPS = two-phonon states [Colour figure can be viewed at wileyonlinelibrary.com]

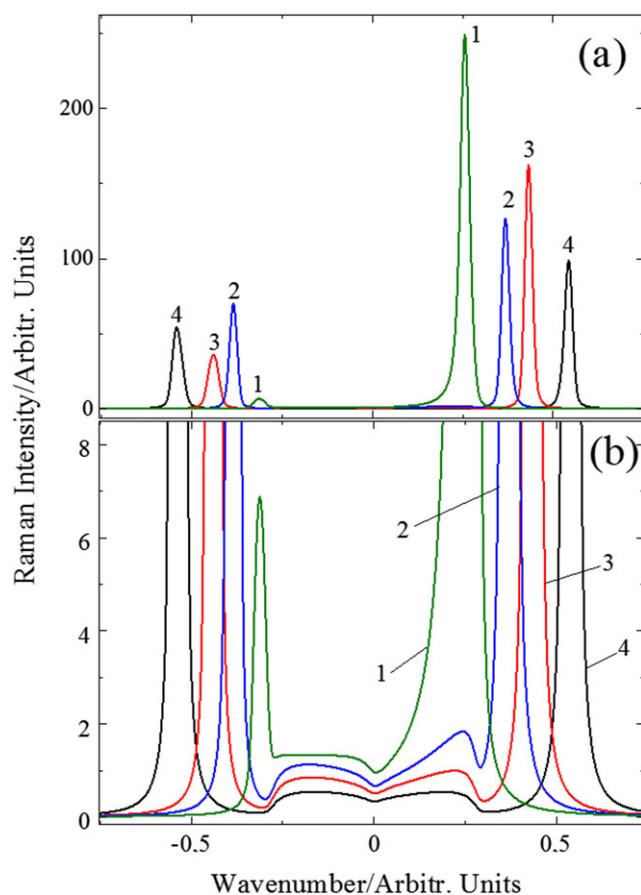


FIGURE 8 (a) Calculated Raman scattering spectra of CO₂ crystal at different values of anharmonic constant Γ responsible for Fermi resonance interaction between the fundamental vibration ω_c and overtone $2\omega_p$; Curve 1— $\Gamma = 0.1$; Curve 2— $\Gamma = 0.15$; Curve 3— $\Gamma = 0.2$; and Curve 4— $\Gamma = 0.33$; (b) zoom-in of the same spectra as in Figure 8a [Colour figure can be viewed at wileyonlinelibrary.com]

Figure 7 shows the measured by us experimental RS spectrum of CO₂ crystal (Curve 1). The scale of the vertical axis is chosen to demonstrate the presence of weak and wide TPS band; therefore, the strong bands are trimmed. Two additional less intense bands appear in Raman spectra at the frequencies 1,369.3 and 1,254.8 cm⁻¹ because the CO₂ crystal studied contained ~2% of ¹³C isotope. The theoretical spectrum calculated for ¹²C isotope using Equations 11 and 12 (Curve 2) is also shown in Figure 7. The spectrum consists of two very strong bands with the maxima at 1,385 cm⁻¹ (the fundamental vibration ω_c) and 1,275 cm⁻¹ (the overtone $2\omega_p$) as well as rather broad band related to TPS in the spectral range 1315 cm⁻¹ ÷ 1360 cm⁻¹. It should be noted that energies of both intense bands of the Fermi doublet in the spectrum of CO₂ crystal are somewhat downshifted as compared to the corresponding doublet bands recorded for CO₂ molecule, Figure 4. This variance is due to the effect of intermolecular interaction.^[13]

Simulation of theoretical dependences and fitting to the experimental spectrum allows to estimate the real relation between the intensities of all spectral components—narrow strong bands (which are trimmed in the experimental curve) and broad TPS—which take part in FR. Figure 8a,b shows the full-scale and zoomed-in graphs of the spectra calculated at various values of the parameter Γ . One can note that the constants Γ and δ_0 are somewhat smaller than the corresponding values for a free CO₂ molecule (compare with the legend to Figure 4).

In Figure 8a, the nonmonotonic change of band intensities with anharmonic constant Γ variation is clearly seen. This behavior occurs due to the participation of wide TPS band in anharmonic interactions.

In Figure 8b, the same spectra are shown in a larger scale. It is seen that TPS band and sharp peak on its low-energy edge (Curve 1) have the same origin. This statement contradicts to the conclusion done in the experimental work,^[35] where it was stated that the formation of TPS (biphonon) is caused by a pair of strong bands: fundamental and overtone. According to the results shown in Figure 8b, the overtone and TPS broad band emerge simultaneously: The biphonon peak is split off from the broad TPS band only at sufficiently large values of anharmonic constant Γ . The intensity of biphonon grows with Γ and becomes comparable with the intensity of the fundamental band.

One can also see that at small Γ (Curve 1), the fundamental band is anomalously broad. This broadening is caused by Fano resonance^[36]: The narrow fundamental band that coincides with a quasicontinuous spectrum (e.g., TPS band) becomes asymmetric and anomalously broadened.

6 | CONCLUSION

We have studied the effects of anharmonic interaction between a fundamental vibration and an overtone (combination tone) both in a separate molecule and in a crystal formed by the same molecules. The detailed analysis revealed the trends of vibrational spectra variation in molecules and solids with the change of important theoretical parameters Γ and A^p that describe the contributions of the third- and fourth-order anharmonism. The theoretical approach provided the spectral positions, intensities, and line shapes of vibrational bands.

For the first time, FR features of a separate molecule and a related crystal built of the same molecules were described in the framework of the same theoretical approach. The theoretical analysis shows that in the case of crystals, FR phenomenon is more complicated due to the participation of the whole band of TPS in the resonance interactions. The spectral features in solid are the fundamental vibration band, overtone, and the TPS band. The ratio between the intensities of overtone (biphonon) and broad band of TPS depends on the ratio Γ/δ_0 (where δ_0 is the difference between the unperturbed states involved in FR). If $\Gamma/\delta_0 > 1$, two strong bands and one very weak broad band are observed in the spectrum similarly to the spectrum of a molecule. But if $\Gamma/\delta_0 < 1$, only one strong fundamental band dominates, and sufficiently broad TPS structure with narrow maximum is observed near the fundamental peak.

Using the above approach, we explored the effects of anharmonism in the spectra of CO_2 molecule and CO_2 molecular crystal and compared with the measured experimental spectra. Pretty good agreement was obtained. The general theoretical approach proposed can also be used to interpret the bands in Raman and IR spectra of various complex molecules and crystals.

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REFERENCES

- [1] I. Hanson, *Phys. Rev.* **1934**, 46(2), 122, <https://doi.org/10.1103/PhysRev.46.122>
- [2] A. Langseth, *Phys. Rev.* **1934**, 46(12), 1057, <https://doi.org/10.1103/PhysRev.46.1057>
- [3] B. T. Darling, D. M. Dennison, *Phys. Rev.* **1940**, 57(2), 128, <https://doi.org/10.1103/PhysRev.57.128>
- [4] A. E. Douglas, D. Sharma, *J. Chem. Phys.* **1953**, 21(3), 448, <https://doi.org/10.1063/1.1698927>
- [5] M. P. Lisitsa, B. N. Malinko, *Opt. Spectrosc.* **1958**, 4, 455.
- [6] E. K. Plyler, N. C. Allen, E. D. Tidwell, *J. Res. Natl. Bur. Stand.* **1957**, 58(5), 255, <https://doi.org/10.6028/jres.058.032>
- [7] E. Fermi, *Z. Phys.* **1931**, 71(3-4), 250, <https://doi.org/10.1007/BF01341712>
- [8] M. Y. Valakh, A. P. Litvinchuk, V. M. Dzhagan, V. O. Yukhymchuk, A. M. Yaremko, Y. A. Romanyuk, M. Guc, I. V. Bodnar, A. Perez-Rodriguez, D. R. T. Zahn, *J. Phys. Condens. Matter* **2016**, 28, 065401(6), 065401, <https://doi.org/10.1088/0953-8984/28/6/065401>
- [9] M. P. Lisitsa, G. G. Tarasov, A. M. Yaremko, *Fiz. Tverd. Tela (Russia)* **1977**, 19, 1122.
- [10] M. P. Lisitsa, A. M. Yaremko, *Journ. Prikladnoj Spectroscopii (Russia)* **1981**, 35, 654.
- [11] V. S. Gorelik, G. G. Mitin, M. M. Sushchinski, *J. Sov. Phys. JETP* **1971**, 61, 656.
- [12] A. M. Yaremko, D. I. Ostrovski, *J. Phys. Condens. Matter* **1995**, 7(40), 7833, <https://doi.org/10.1088/0953-8984/7/40/014>
- [13] M. P. Lisitsa, A. M. Yaremko, *Resonance Fermi (in Russian)*, Naukova Dumka, Kiev **1984**.
- [14] G. M. Gale, P. Gujot-Sionnest, W. Q. Zheng, C. Flytzanis, *Phys. Rev. Lett.* **1985**, 54(8), 823, <https://doi.org/10.1103/PhysRevLett.54.823>
- [15] O. Sode, M. Keceli, K. Yagi, S. Hirata, *J. Chem. Phys.* **2013**, 138, 074501(7), 074501, <https://doi.org/10.1063/1.4790537>
- [16] G. Cardini, V. Schettino, *J. Chem. Phys.* **2014**, 140(17), 177101, <https://doi.org/10.1063/1.4873690>
- [17] S. Hirata, O. Sode, M. Keceli, K. Yagi, J. Li, *J. Chem. Phys.* **2014**, 140(17), 177102, <https://doi.org/10.1063/1.4873692>
- [18] K. Li, J. Cheng, Q. Ye, Y. He, J. Zhou, K. Cen, *Bioresour. Technol.* **2017**, 244(Pt 2), 1439, <https://doi.org/10.1016/j.biortech.2017.04.116>
- [19] N. Liu, C. Aymonier, C. Lecoutre, Y. Garrabos, S. Marre, *Chem. Phys. Lett.* **2012**, 551, 139, <https://doi.org/10.1016/j.cplett.2012.09.007>
- [20] B. S. K. Sharma, A. K. Misra, S. M. Clegg, J. E. Barefield, R. C. Wiens, T. Acosta, *Phil. Trans. R. Soc. A* **2010**, 368(1922), 3167, <https://doi.org/10.1098/rsta.2010.0034>
- [21] L. Chen, H. Lu, J. A. Ripmeeste, *Chem. Eng. Sci.* **2015**, 138, 706, <https://doi.org/10.1016/j.ces.2015.09.001>
- [22] D. Feng, Y. Zhao, Y. Zhang, S. Sun, *Int. J. Hydrog. Energy* **2017**, 42(18), 13070, <https://doi.org/10.1016/j.ijhydene.2017.04.018>
- [23] T. Li, L. Zhang, L. Dong, S. Wang, Y. Song, L. Wu, C.-Z. Li, *Fuel* **2017**, 195, 253, <https://doi.org/10.1016/j.fuel.2017.01.076>
- [24] H. M. Lamadrid, L. R. Moore, D. Moncada, J. D. Rimstidt, R. C. Burruss, R. J. Bodnar, *Chem. Geol.* **2017**, 450, 210, <https://doi.org/10.1016/j.chemgeo.2016.12.034>
- [25] T. Kobayashi, J. Yamamoto, T. Hirajima, H. Ishibashi, N. Hirano, Y. Lai, V. S. Prihod'ko, S. Arai, *J. Raman Spectrosc.* **2012**, 43(8), 1126, <https://doi.org/10.1002/jrs.3134>
- [26] R. S. Barlow, G. Magnotti, H. C. Cutcher, A. R. Masri, *Combust. Flame* **2017**, 179, 117, <https://doi.org/10.1016/j.combustflame.2017.01.027>

- [27] S. Braeuer, J. J. Schuster, M. T. Gebrekidan, L. Bahr, F. Michelino, A. Zambon, S. Spilimbergo, *Foods* **2017**, 6(5), 37, <https://doi.org/10.3390/foods6050037>
- [28] H. Ratajczak, A. M. Yaremko, *Chem. Phys. Lett.* **1999**, 314(1-2), 122, [https://doi.org/10.1016/S0009-2614\(99\)01107-0](https://doi.org/10.1016/S0009-2614(99)01107-0)
- [29] D. M. Dennison, *Rev. Mod. Phys.* **1940**, 12(3), 175, <https://doi.org/10.1103/RevModPhys.12.175>
- [30] Q. Zhu, A. R. Oganov, C. W. Glass, H. T. Stokes, *Acta Cryst* **2012**, B68, 215.
- [31] W. G. Fateley, F. R. Dollish, N. T. McDevitt, F. F. Bentley, *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations: The Correlation Method*, Wiley-interscience, New York **1972**.
- [32] H. Ratajczak, A. M. Yaremko, J. Baran, *J. Mol. Struct.* **1992**, 275, 235, [https://doi.org/10.1016/0022-2860\(92\)80199-R](https://doi.org/10.1016/0022-2860(92)80199-R)
- [33] A. M. Yaremko, V. O. Yukhymchuk, S. S. Ponomaryov, V. V. Koroteev, V. M. Dzhagan, Y. A. Romanyuk, J. Baran, *Sol. St. Commun.* **2014**, 195, 39, <https://doi.org/10.1016/j.ssc.2014.06.020>
- [34] V. M. Agranovich, *Fiz. Tverd. Tela (Russian)* **1970**, 12, 562.
- [35] K. R. Witters, E. J. Cahill, *J. Chem. Phys.* **1977**, 66(6), 2755, <https://doi.org/10.1063/1.434229>
- [36] U. Fano, *Phys. Rev.* **1961**, 124(6), 1866, <https://doi.org/10.1103/PhysRev.124.1866>

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