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B202

Self-Focusing in SF_6

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Abstract

We show by explicit calculation of our previously published quasicontinuum model that the molecular susceptibility rapidly approaches zero as higher excited states of the molecule become populated. Hence the overtones of the ν_3-pumped mode are totally responsible for the self focusing effects in SF_6. We explicitly calculate the ν_3 ladder contribution to the susceptibility. Our vibrational model is a classical triply degenerate anharmonic oscillator in the Cartesian basis with the anharmonicity parameters chosen to be consistent with the latest spectroscopic analysis of the $3\nu_3$ overtone spectrum. The rotational structure is represented by a distribution of these oscillators where the distribution is chosen to correspond to the spectrum of the ν_3 fundamental. We find good agreemnt with the 300° in self-focusing data of Nowak and Ham at CO_2 P(28), P(20) and P(10) in SF_6.

I. ν_3-ladder contribution

Nowak and Ham[1] have recently reported strong self-focusing and self-defocusing in SF_6 vapor. Their data are in agreement with previous measurements,[2] but are considerably more detailed. Qualitatively, their data show focusing on the blue side of the 300° K ν_3 absorption feature and defocusing on the red side. However, as the laser power is increased at P(20) (a red side curve which shows defocusing at low power) they begin to observe focusing. The transition occurs in the region 10^{-2}-10^{-1} J/cm². This observation is presumably due to the anharmonic red-shift of the higher vibrational resonances, i.e., as the power is increased and the excitation moves higher in the molecule the absorption feature shifts toward the red such that the P(20) laser line changes its location from the red to the blue side of the absorption feature.[1]

In section II we show that the quasicontinuum region of large polyatomic molecules cannot be responsible for self-focusing due to its inherent broad resonant character. Therefore, we calculate the ν_3 ladder contribution to the susceptibility in SF_6 and show that it accounts for all the observations of Nowak and Ham.[1]

Our model of the vibrational structure of the ν_3 ladder in SF_6 is a triply degenerate anharmonic oscillator with the Hamiltonian expressed in the Cartesian basis. We choose this basis because it allows a physical picture of the molecule, and because it gives a good description of the molecular energy levels in agreement with the latest spectroscopy and analysis of the $3\nu_3$ overtone in SF_6.[3] We assume the predominant effect of rotations is to introduce an inhomogeneous dephasing on the vibrational spectrum. Therefore, the total response of the molecule to the field is calculated by summing the vibrational response for each rotational line in the entire 300° K spectrum of the ν_3 fundamental at low power weighted by the relative intensity of the line. The area under the curve is normalized to unity. Since the effect of hotbands is to introduce new ν_3 ground states, we do not distinguish their contribution to the absorption profile as all "ground" states contribute equally.

The vibrational Hamiltonian in the Cartesian basis is

$$H = \sum_{i}^{3} \frac{p_i^2}{2m} + \frac{m\omega_0^2}{2} x_i^2 + \hbar(X_{33}-6T_{33})\left(\frac{m\omega_0}{\hbar}\right)^2 \left(\sum_i x_i^2\right)^2$$

$$+ 10\hbar T_{33}\left(\frac{m\omega_0}{\hbar}\right)^2 \sum_i x_i^4 - e \sum_i x_i \mathcal{E}_i \cos\omega t \qquad (1)$$

where the parameters X_{33} and T_{33} are determined from Table II of Patterson, Krohn and Pine[3] to be

$$X_{33} = -\text{[illegible]}\ \text{cm}^{-1} \qquad (2a)$$

B202

$$T_{33} = -.31025\ \mathrm{cm}^{-1} \tag{2b}$$

The unperturbed resonant frequency of the oscillator is ω_0. The laser amplitude and frequency are E_i and ω, respectively. The charge, e, and mass, m, will not appear in our final results and are removed using the relation

$$e^2\hbar/4\mu^2\omega_0 m \equiv 1 \tag{3}$$

where μ is the transition dipole moment equal to 0.4 Debye.[4]

The equation of motion for the ith Cartesian coordinate is calculated from (1) in the usual way:

$$\ddot{x}_i + 2\gamma\dot{x}_i + \omega_0^2 x_i + (X_{33}-6T_{33})\ \frac{4m\omega_0^2}{\hbar}\left(\sum_j x_j^2\right) x_i$$

$$+\ 40T_{33}\ \frac{m\omega_0^2}{\hbar}\ x_i^3 = \frac{e}{m}\ E_i\ \cos\ \omega t\quad , \tag{4}$$

where we have introduced a small decay parameter, γ, so that the susceptibility does not become infinite on resonance. Since self-focusing effects are due to the part of the susceptibility which is proportionalto the driving field at frequency ω, we look for a solution for x_i of the form

$$x_i = \frac{1}{2}\left(c_i e^{i\omega t} + c_i^* e^{-i\omega t}\right) \tag{5}$$

where a complete solution for x_i would contain all harmonic frequencies. We can neglect their contribution in (5) since the harmonic coefficients have resonant denominators which are large only in the region of the harmonic resonance. The validity of using (5) and dropping all harmonic terms has been explicitly checked by exact integration for a single anharmonic oscillator.[5]

After substituting (5) into (4) and neglecting the higher harmonic terms we obtain the equations for each Cartesian coefficient:

$$\left[\Delta - i\gamma + (X_{33}-6T_{33})\ \frac{m\omega_0}{\hbar}\ \sum_j |c_j|^2 + 15T_{33}\ \frac{m\omega_0}{\hbar}|c_i|^2\right]c_i^*$$

$$+\ (X_{33}-6T_{33})\ \frac{m\omega_0}{2\hbar}\ \sum_j\ (c_j^*)^2 c_i = \frac{e}{2m\omega_0}\ E_i \tag{6}$$

where we have assumed $\omega+\omega_0 \approx 2\omega_0$ and $\Delta = \omega_0-\omega$. We have found that if the field is oriented along an arbitrary direction in the molecule, then the polarization is along some other direction where the susceptibility is computed from the projection of the coordinate along the direction of the field. However, if the field is oriented along a symmetry axis of the molecule, then the polarization is only along that axis. The solution of (6) in this case is easily obtained for the coordinate and therefore for the susceptibiltiy and is a generalization of the result for a simple anharmonic oscillator:

$$\chi = \frac{N\mu^2}{\hbar}\left[\frac{1}{\Delta + (?/8)\Xi_{33} Q - i\gamma}\right] \tag{7}$$

and

$$Q = \frac{4\Omega^2}{(\Delta + (3/8)\Xi_{33} Q)^2 + \gamma^2} \tag{8}$$

where Ω is the Rabi frequency, Ξ_{33} is the anharmonicity of the oscillator along a symmetry axis and N is the molecular density. The variable Q is evaluated from (8), and the solution substituted into (7) gives the susceptibility. The value of Ξ_{33} along each the symmetry axis is

B202

$$Z_{33} = X_{33} - \frac{8}{3} T_{33} = -.87 \tag{9a}$$

$$X_{33} - T_{33} = -1.39 \tag{9b}$$

$$X_{33} + 4T_{33} = -2.94 \tag{9c}$$

where these symmetry axis oscillators can be isolated in Fig. 15 of Ref. 3 and shown to be a good representation of the vibrational structure of SF_6 molecule. It is interesting to notice the structure of (7) with respect to the variable Q as defined in (8). As the laser power increases in (8), Q increases in a nonlinear fashion with a magnitude determined by the anharmonicity. Since Z_{33} is negative, the resonance character in (7) is shifted toward the red with increasing power. This quantitative result is in agreement with the qualitative discussion given in the introduction. We should also note that the susceptibility calculated here and that for a two-level model[4] are markedly different in this respect.

The rotational structure for this calculation is represented by an inhomogeneous broadening of the vibrational molecule. We, therefore, calculate the total susceptibility of the ν_3 absorption band by summing a collection of vibrational molecules of different harmonic frequencies and band strengths chosen according to the 300° K ν_3 absorption spectrum.[7a] Our synthesis of the spectrum is shown in Fig. 1. The only free parameter in this work is γ which we have chosen to give the correct cross section vs. fluence dependence shown in Fig. 2 at several frequencies.[7b] Since the band is roughly 20 cm^{-1} wide, the calculated susceptibility is independent of this one free parameter.

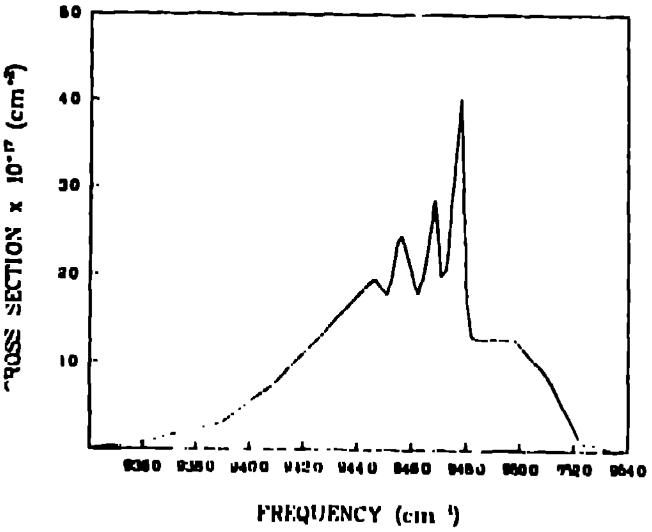
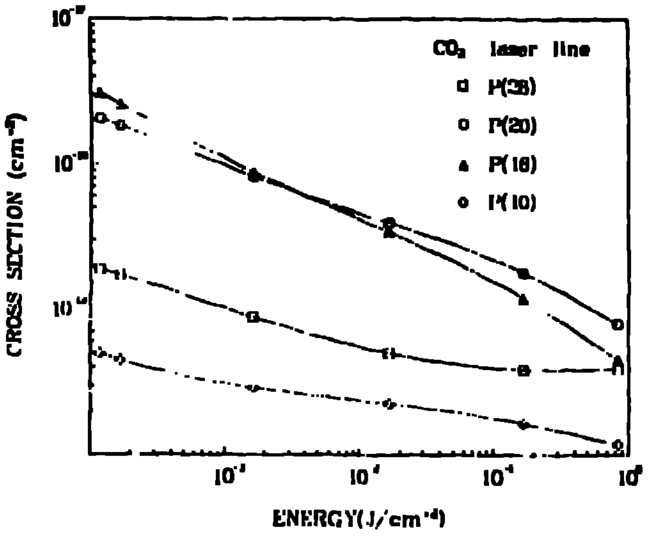


Figure 1. Synthesized FT-IR scan of absorption cross section vs. frequency for SF_6 at 300° K.

In Fig. 3 we show the calculated susceptibility vs. fluence at several frequencies studied by Nowak and Ham.[1] Our calculations are inherently intensity dependent such that the fluences used in the figures are computed from intensities assuming a 1.6 ns square pulse, i.e. 10^{-2} J/cm^2 = 6.25 MW/cm^2. While a precise comparison of the susceptibility curves with the data can only be made after performing a two dimensional propagation calculation based on Figures 2 and 3, we feel the qualitative agreement is excellent and worthy of presentation in this preliminary form. We interpret the susceptibility curves assuming a positive (negative) slope implied focusing (defocusing).[4,5] We find a gradual defocusing at CO_2 P(28), a red side curve in the region where the data exists, i.e. $E \leq 1$ J/cm^2. At CO_2 P(20) we observe a transition from defocusing to focusing in the region between 10^{-2} and 10^{-1} J/cm^2. We find the strongest focusing effect at CO_2 P(16) at the Q-branch of the low fluence absorption feature (not shown). At P(10) we find a continuous trend always towards a focusing effect. Our results are qualitatively in good agreement with the Nowak and Ham data.[1] However, we do find that this susceptibility function always gives a slightly higher power than the observed data to see the same effect.[1] We expect this discrepancy between the susceptibility curves and the data since absorption in the wings of the beam, has not been taken into account in plotting the data, i.e. beam radius vs. fluence at a fixed positioned detector, always will show a "focusing" effect at lower laser intensities.

B202



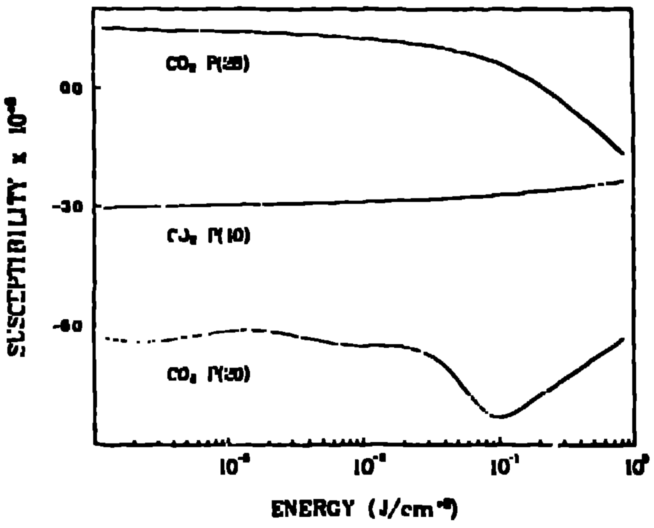


Figure 2. Cross section vs. fluence for four CO_2 laser frequencies P(10), P(16), P(20), and P(28). The parameter γ is fit from P(20) data, $\gamma=0.008$ cm^{-1}. The change in slope above 5×10^{-2} J/cm^2 results from the QC not being included in the calculation.

Figure 3. Real part of the susceptibility vs. fluence for three CO_2 laser frequencies P(10), P(20), and P(28). The density for all three curves has been fixed at 10^{15}/cc since it only results in a systematic shift of the curves. However, the data of Ham and Nowak were actually taken at three different pressures in the range 0.3-1 torr.

II. Quasicontinuum contribution

Our model of the molecular quasicontinuum is characterized by rapid intramolecular V-V relaxation, leading the Fermi Golden Rule widths of the laser pumped levels and statistical equilibration of excited populations on a timescale short compared with molecular pumping rates.[11] The model was calibrated against absorption data taken by Deutsch[11] and for laser powers below or equal to 100 MW/cm^2 the statistical equilibration hypothesis was found to be self consistent.

Consider a molecular excitation at energy $n\nu_3$. We denote the degenerate manifolds at $n\nu_3$ by their ν_3-content and consider the V-V rates to couple only states differing in ν_3 by one quantum. Bloch equations describing the absorption and dispersion for a laser transition from the k^{th} (ν_3-content) manifold of $n\nu_3$ to the $(k+1)^{th}$ manifold at $(n+1)\nu_3$ are[11]

$$\dot{u}_k(n) = -\Delta_k(n)v_k(n) - \gamma_k(n)u_k(n) \qquad (10)$$

$$\dot{v}_k(n) = \Delta_k(n)u_k(n) - \gamma_k(n)v_k(n) + \Omega_k(n)w_k(n) \qquad (11)$$

with $\Delta_k(n)$ the detuning and γ_k the V-V relaxation rate.

$$\gamma_k(n) = 2\pi\alpha^2[D_{k+1}(n) + D_{k-1}(n) + D_k(n+1) + D_{k+2}(n+1)] \qquad (12)$$

In Eq. (12) α is the anharmonic coupling and $D_k(n)$ are the subdensities of states having $k\nu_3$ at energy $n\nu_3$ in the molecule, and in Eq. (11) $\Omega_k(n)$ is the effective QC Rabi pumping frequency.[illegible] The inversion, [illegible] is found from the population distribution at the given laser intensity and the statistical equilibration hypothesis.

B202

$$w_k(n) = (D_{k+1}(n+1)/D(n+1))P_{n+1} - (D_k(n)/D(n))P_n \quad , \tag{13}$$

where D(n) is the total molecular density of states. For intensities less than 100 MW/cm^2 we have found that V-V relaxation dominates the laser pumping and we have constructed the absorption cross sections from $v_k(n)$, Eq. (11), in steady state.[18] The molecular susceptibility for this transition is gotten, correspondingly from the steady state solution for $u_k(n)$:

$$u_k(n) = -[\Omega_k(n)\Delta_k(n)/(\Delta_k^2(n) + \gamma_k^2(n))]w_k(n) \quad , \tag{14}$$

and

$$\chi_k(n) = (N\hbar\Omega_k(n)/E^2)u_k(n) \quad . \tag{15}$$

Here N is the density of molecules (10^{18}/cm^2 at 0.28 torr and 300° K, used in our calculations) and E is the laser electric field amplitude. Note that Ω_k is linear in E so that the only field dependence in $\chi_k(n)$ is from the $w_k(n)$, i.e. the excited state populations. The total QC susceptibility is simply the sum of the $\chi_k(n)$ over all QC states. Fig. 4 shows the total QC susceptibility as a function of laser power up to 20 MW/cm^2 at a frequency of 944 cm^{-1} corresponding to CO_2-P(20).

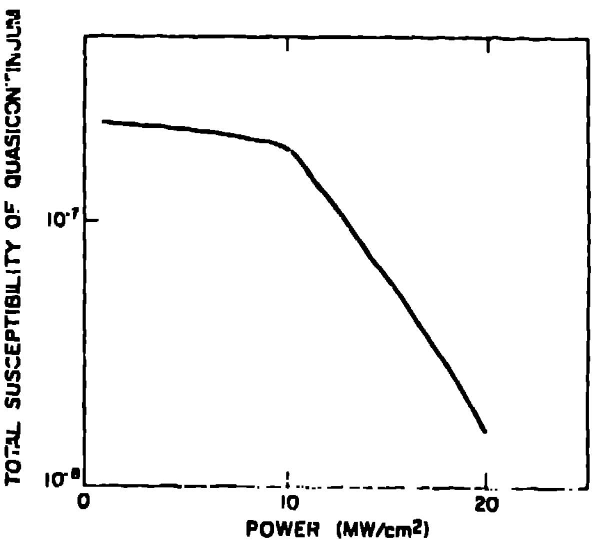


Figure 4. Molecular susceptibility from the quasicontinuum model of Ref. 10, vs. laser power. Laser line is CO_2P(20) and SF_6 gas is at 0.29 torr at 140° K. Quasicontinuum contributions are much smaller than ν_3-ladder contributions in self-focusing power region.

Population distributions at the various laser powers were found from our previous modeling efforts.[18] We see in the figure a rapid falloff in χ with increased laser power. The reason for this is simply the fact that as the energy increases, the widths $\gamma_k(n)$ dominate detunings and the partial susceptibilities, $\chi_k(n)$, decrease as $1/\gamma_k(n)$. The dramatic falloff of the total susceptibility with increasing laser intensity is due to the increasing population of high n-states. However, the absolute value of the rate of change is still far to small to contribute. The absorption term of Eq. (11), $v_k(n)$, does not falloff however since it is related to $u_k(n)$ by $(\gamma_k(n)/\Delta_k(n))$, a large factor for most QC states. Hence, our previous model gives a picture of broadened QC-states leading the dramatic decrease in polarization, $u_k(n)$, while the absorption is seen to increase approximately linearly[17] (high QC).

Even though this result was arrived at on the basis on a particular model of the molecular quasicontinuum, we feel that it will be shown to be a property of all models featuring strong V-V relaxation and resonant absorption. In SF_6 there are only two modes, ν_3 and ν_4 which carry a dipole moment and can therefore lead to macroscopic polarization. Intramolecular V-V relaxation, if statistical, will means a rapid flow of the excitation into background modes which in general will not add to the polarization, but instead lead to dilution of the susceptibility. We expect that molecules with large densities of states and couplings into those densities will show diminished self focusing effects. The effect should be entirely absent in a molecule like S_2F_{10} which is thermally in its QC at room temperature.[4] Furthermore in two color multiphoton experiments if the first laser is powerful enough to put all the molecules into the QC, then we would expect to observe only weak focusing or defocusing effects of the second laser.

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B202

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