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Model for the linear- and nonlinear-optical properties of β-quinol clathrates

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We present a theoretical model for the optical activity of clathrates in the far infrared, based upon a Pöschl-Teller potential fit to the intermolecular guest-host potential. Experimental comparisons of the absorption coefficient and predictions of the third-order susceptibility for frequency tripling are made for the argon clathrate.

INTRODUCTION

In this paper we examine the infrared activity of rattling motion in β-quinol clathrates, which are a type of molecular inclusion compound. Comparisons with experimentally measured linear absorption coefficients and predictions for nonlinear-optical response in the far infrared are made for the β quinol:Ar system.

Inclusion compounds are two-component molecular complexes in which one component, the host, forms a lattice structure containing large voids in which the second component, the guest, is trapped. When the inclusions are confined in three dimensions, the inclusion compounds are known as clathrates.

The β-hydroquinone, or β-quinol, system is studied because of the availability of data in the large volume of literature and because of the ease with which this material can be prepared and stored. The β-crystalline modification of hydroquinone is a metastable crystalline phase which becomes stable when gas molecules are introduced into the cages. The crystals are prepared by slow cooling of a saturated solution, and the guest molecules are introduced either as the solvent, dissolved in the solvent, or by placing the solution in a high-pressure vessel, if the guest is normally gas phase.

Hydroquinone $[C_6H_4(OH)_2]$ is formed by a benzene ring with diametrically opposed hydroxyl groups. The β-crystalline form is composed of two interpenetrating sublattices with the hydroquinone molecules hydrogen bonded together at the OH groups. In each sublattice one OH group of six different molecules bond end to end to form a hexagonal oxygen ring. Consecutive hydroquinone molecules are directed above and below the plane of the hexagon at approximately 45°, with the other OH group of each molecule participating in the formation of a separate oxygen ring.

The cage is bounded on top and bottom by oxygen rings of the different sublattices with the equatorial boundary formed by 12 carbon atoms and six hydrogen atoms from six different hydroquinone molecules arranged with the point-group symmetry S_6. A diagram of the structure is given in Fig. 1.

The motion of the enclathrated or guest molecule in the host lattice has been extensively studied using a variety of methods, including thermodynamic studies,[1-6] dielectric relaxation,[7-10] infrared,[11,12] far infrared,[13,14] Raman,[15-18] and Mössbauer[19] spectroscopy, nuclear magnetic,[20-23] nuclear quadrupole,[24] and electron paramagnetic[25] resonance, magnetic susceptibility[26-29] and neutron[30] and x-ray[31-33] scattering. The motion of the guest depends greatly upon the type of molecule involved. Many molecules can be treated as essentially isolated in their cages, with the lattice screening decoupling its motion from that of its neighboring guests. Some polar molecules can be strongly coupled through their dipolar interaction or possibly by a lattice-mediated interaction;[34] however, we will not be considering these interactions in this paper.

The guest-host interaction is comprised of the Lennard-Jones potentials between atoms of the inclusion and atoms in the cage walls, and the interaction of any multipole moments of the inclusions with the dipole moments of the OH groups and the quadrupole moments of the benzene rings. Inclusions such as the noble gases exhibit only translational motion, whereas diatomics and small polyatomics will also exhibit rotational-liberational motion. Sepecta in the far-infrared reveals lines due to both this translational or rattling motion and the hindered rotational motion.

In 1957 van der Walls[1] presented a statistical mechanical theory of the thermodynamic properties of noble gas clathrates. He assumed classical motion of the atom in a sphericalized Lennard-Jones potential, and although his theory was very successful in explaining high-temperature properties, such as stabilization of the β-crystalline form by clathration, the guest contribution to

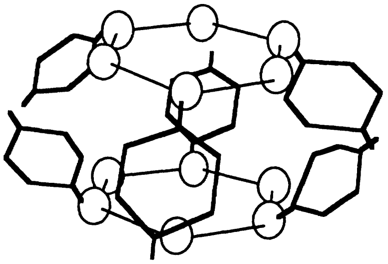

FIG. 1. Cage structure of β-hydroquinone, where open circles are oxygen atoms, bold hexagons are benzene rings of the hydroquinone molecule, and the hydrogen atoms are not shown.

the low-temperature specific heat was incorrect. This deviation is to be expected from any classical theory.

Attempts were made to extend this theory to low temperature by approximating the potential by a best-fit spherical harmonic-oscillator potential. However, the anharmonicity in the energy spectrum causes deviation in the specific heat at moderate and high temperatures.

Another approach used by Neece and Poirier[6] was to fit the potential to a symmetric Pöschl-Teller potential, which is an anharmonic two-parameter function. This potential may be written for a guest of mass m as

$$V(x,y,z)=\sum_{i=1}^{3}\frac{m\omega_i^2}{2}\left[\frac{2\gamma_i}{\pi}\right]^2\tan^2(\pi,x_i/2\gamma_i)\ , \tag{1}$$

where ω_i is the frequency in the harmonic approximation $(\gamma_i\rightarrow\infty)$ and γ_i is the potential width. The reason for using this potential is that an exact solution to the Schrödinger equation can be found. Although the symmetry of the potential is D_{2h}, becoming O_h when $\gamma_1=\gamma_2=\gamma_3=\gamma$ and $\omega_1=\omega_2=\omega_3=\omega_0$, it was assumed that with the proper choice of parameters the mismatch with the symmetry of the cage should not introduce an unreasonable amount of error. Neece and Poirier used the O_h symmetry version of the potential and chose the parameter γ from cage dimensions and van der Waals radii, and the parameter ω_0 to fit the data. The predicted specific heat agreed very well for the noble gases.

Simultaneously another group, Burguel *et al.*[13] used the same potential to fit the "rattling" spectra of the noble gases and small diatomic molecules. The values of the potential parameters obtained by this method agreed reasonably well with the values of Neece and Poirier obtained from thermodynamic measurements.

A more rigorous attempt to explain the motion of small inclusions, that of Hirokawa,[35-38] was to write out the sum of Lennard-Jones and multipole-multipole interactions and then to solve for the motion in the potential expanded to second order in the equilibrium displacement with a quartic perturbation. However, the large vibrations of the cage atoms, as evidenced by the large linewidths of the translational transitions, will make the exact details of the cage symmetry unimportant. Thus, since the exact symmetry of the potential is not essential, it will be advantageous to choose a potential which is more theoretically tractable than that used by Hirokawa, yet still contains the essential details of the inclusion motion responsible for optical interactions.

We will therefore use a symmetric (O_h) Pöschl-Teller potential to model the interaction and explain the optical activity of the translational motion of charge-neutral species. We then calculate the linear absorption coefficient and, because of the favorable comparison with experiment, we use this model to predict third-order nonlinear susceptibility for third-harmonic generation. Since rotation is being neglected, the results derived here are assumed to correspond most closely to the rare gas clathrates and will be specifically compared to the argon clathrate, although we also anticipate applicability to small nonpolar molecules at low temperatures that see an inversion-symmetric potential.

INFRARED ACTIVITY OF RATTLING MOTION

Translational motion of a neutral atom under normal circumstances is uncoupled from infrared radiation. However, when the atom is confined in a potential whose variation over the extent of the atom is significant, a dipole moment will be induced in the atom. This dipole moment can then couple to the radiation field, allowing transitions between the bound translational or "rattling" states to be optically induced.

In this section we model the atom cage potential as a three-dimensional Pöschl-Teller potential with O_h symmetry and consider the first-order variation of the potential as a perturbation which induces an asymmetric charge distribution in the atom. We will then show how these wave functions couple rattling states to the optical field.

In this model it is assumed that the sum of the interactions of the guest atom and the cage atoms can be approximated by a Pöschl-Teller potential. We also assume that this potential is comprised of a sum of interactions of each electron in the atom, and that each electron, screening one unit of nuclear charge, sees a Pöschl-Teller potential of varying strength. The Hamiltonian of the atom in the cage, therefore, is written as the sum of the internal or free atom Hamiltonian (H_A), the kinetic energy of the center of mass, and the sum of the single-electron potentials

$$H=H_A+\frac{P^2}{2m}+\sum_{i=1}^{3}\sum_{\beta=1}^{Z}\frac{S_\beta m\omega_0^2}{2}\left[\frac{2\gamma}{\pi}\right]^2\tan^2[\pi(R_i+r_i^\beta)/2\gamma]\ , \tag{2}$$

where S_β is the strength of the interaction of the βth electron, such that

$$\sum_{\beta=1}^{Z}S_\beta=1\ , \tag{3}$$

R_i is the ith component of the center of mass, and r_i^β is the ith component of the position of the βth electron relative to the center of mass.

Since we are considering a noble gas inclusion, specifically argon, we can get an idea of what values the S_β's should have. The ground state of argon is a $3p^6\,{}^1S_0$ state lying 15.8 eV below ionization, while the first excited states are $3p^5 4s^1$ lying from 4.2 to 3.9 eV below ionization.[39] Examination of the spectra shows that all of the excited states below about 1 eV from ionization are $3p^5 nl^1$ states, with multiple electron excitation states, if they exist at all, lying very near ionization.

Thus all important excited states of the charge neutral atom are single-electron promotion or $3p^5 nl^1$ states. The atom-cage interaction, therefore, is due to coupling to single-electron excitation states and only one particular S_β will be significant, while all others are negligible.

Also, the dipole moments between the ground and excited states will be due to a single-electron position, and we can therefore write the position of the promoted electron as the sum of all electron positions,

$$r_i^{\beta'}=\sum_{\beta=1}^{Z} r_i^{\beta}=d_i \ , \tag{4}$$

keeping in mind that when we take matrix elements only a single electron will contribute.

Expanding to first order in the electron positions, the resulting Hamiltonian becomes

$$\begin{aligned} H=H_A+\frac{P^2}{2m}+\sum_{i=1}^{3}\frac{m\omega_0^2}{2}\left(\frac{2\gamma}{\pi}\right)^2\tan^2(\pi R_i/2\gamma) \\ +\sum_{i=1}^{3} m\omega_0^2\left(\frac{2\gamma}{\pi}\right)\frac{\sin(\pi R_i/2\gamma)}{\cos^3(\pi R_i/2\gamma)}d_i \ , \end{aligned} \tag{5}$$

which is the sum of the atomic and center-of-mass Hamiltonians and a perturbation which couples the two. The values of the parameters ω_0 and γ will be chosen to match the energy spectrum with the observed far-infrared transition frequencies.

The eigenfunctions of the Pöschl-Teller potential are

$$\begin{aligned} \psi_n(x)=2^{\alpha-1}\Gamma(\alpha)\left[\frac{(n+\alpha)n!}{\gamma\Gamma(n+2\alpha)}\right]^{1/2} \\ \times\cos^{\alpha}(\pi x/2\gamma)C_n^{(\alpha)}(\sin\pi x/2\gamma) \ , \end{aligned} \tag{6}$$

where $C_n^{(\alpha)}(\omega)$ are Gegenbauer or ultraspherical polynomials , and the parameter α is given by

$$\alpha=\frac{1}{2}\left\{1+\left[1+\frac{4m^2\omega_0^2}{\hbar^2}\left(\frac{2\gamma}{\pi}\right)^4\right]^{1/2}\right\} \ , \tag{7}$$

with the energy eigenvalues

$$E_n=\frac{\hbar^2}{2m}\left(\frac{\pi}{2\gamma}\right)^2[(n+\alpha)^2-\alpha(\alpha-1)] \ . \tag{8}$$

To first order in the perturbation the wave functions become

$$\begin{aligned} |\psi_{a,\{n_i\}}\rangle=|a,\{n_i\}\rangle \\ -\sum_{i=1}^{3}\frac{m\omega_0^2}{\hbar}\left(\frac{2\gamma}{\pi}\right) \\ \times\sum_{b,\{k_i\}}\frac{|b,\{k_i\}\rangle\langle b|d_i|a\rangle\varepsilon_{kn}^{i}}{\omega_{ba}+\omega_{kn}} \ , \end{aligned} \tag{9}$$

with

$$\varepsilon_{kn}^{i}=\left\langle k_i\left|\frac{\sin(\pi R/2\gamma)}{\cos^3(\pi R/2\gamma)}\right|n_i\right\rangle \ . \tag{10}$$

The energy eigenvalues corrected to second order are

$$E_{a\{n\}}=\hbar\omega_\alpha+\sum_{i}\left[\frac{\hbar^2}{2m}\left(\frac{\pi}{2\gamma}\right)^2[(n+\alpha)^2-\alpha(\alpha-1)]-m^2\omega_0^4\left(\frac{2\gamma}{\pi}\right)^2\alpha_{\rm el}^{i}(a)\langle n_i|\varepsilon^2|n_i\rangle\right] \ , \tag{11}$$

where $\alpha_{\rm el}^{i}(a)$ is the electronic polarizability of the state a in the ith direction. As an aside, we note that the atomic transition frequencies of an enclathrated atom will be shifted by a quantity that depends upon the translational state and the difference in polarizabilities of the two atomic states. There will also be a weak violation of the selection rules for the free atom.

To determine the parameters α and γ, we equate the energy differences, including the second-order correction, to the observed translational frequencies for an atom in the ground state. The quantities $\langle n|\varepsilon^2|n\rangle$ have been calculated by direct integration so that the equations for the frequencies of the zero-to-one and the one-to-two transitions are

$$\omega_{10}=\Omega(2\alpha+1)-8\kappa\Omega^3\frac{\alpha^3(\alpha-1)^2(\alpha+2)}{(2\alpha-1)(2\alpha-3)(2\alpha-5)} \ , \tag{12}$$

$$\begin{aligned} \omega_{21}=\Omega(2\alpha+3) \\ -8\kappa\Omega^3\frac{\alpha^2(\alpha-1)^2(2\alpha^3+17\alpha^2+29\alpha+15)}{(2\alpha+1)(2\alpha-1)(2\alpha-3)(2\alpha-5)} \ , \end{aligned} \tag{13}$$

where

$$\Omega=\frac{\hbar}{2m}\left(\frac{\pi}{2\gamma}\right)^2, \quad \kappa=8m\sum_{b}\frac{|\langle a|d_i|b\rangle|^2}{\hbar\omega_{ba}}=8m(\alpha_{\rm el}/e^2) \ , \tag{14}$$

and $\alpha_{\rm el}$ is the electric polarizability of the atomic ground state. The transitional energies for the argon clathrate have been measured[13] to be $\omega_{10}=35.5\ {\rm cm}^{-1}$, and $\omega_{21}=37.0\ {\rm cm}^{-1}$, so that with a polarizability of $1.85\times10^{-40}\ {\rm C^2\,m^2/J}$ (Ref. 40) a Newton's algorithm solution to Eqs. (15) and (16) yields a value of $\alpha=20.25$, and $\Omega=0.876\ {\rm cm}^{-1}$. This can be compared to a value of $\alpha=23.17$, and $\Omega=0.750\ {\rm cm}^{-1}$, which would be obtained by fitting only the zero-order energies to the observed spectra.

Now if we apply an optical field, this will introduce a second perturbation in the Hamiltonian of Eq. (6), which can be written in the form

$$\langle\psi_{a,\{n_i\}}|H'(t)|\psi_{a,\{m_i\}}\rangle=-\boldsymbol{\mu}_{nm}^{\rm eff}\cdot\mathbf{E}\sin(\omega t) \ , \tag{15}$$

with the ith component of the effective dipole moment for transitions in the ith direction given by

$$2em\omega_0^2\left[\frac{2\gamma}{\pi}\right](\alpha_{\mathrm{el}}/e^2)\varepsilon^i_{nm}\ , \tag{16}$$

The translational matrix elements, ε^i_{nm}, of the lowest four transitions, including the zero to three overtone, were found by direct integration to be

$$\varepsilon_{10}=\left[\frac{\Gamma(\alpha)}{\Gamma(\alpha+\frac{1}{2})}\right]^2\frac{\alpha}{(\alpha-1)}\left[\frac{\alpha+1}{2}\right]^{1/2}\ , \tag{17a}$$

$$\varepsilon_{21}=\frac{(4\alpha+5)}{(2\alpha+1)}\left[\frac{(\alpha+2)}{(2\alpha+1)}\right]^{1/2}\varepsilon_{10}\ , \tag{17b}$$

$$\varepsilon_{32}=\left[\frac{20(\alpha+1)(\alpha+2)}{(2\alpha+1)(2\alpha+3)}-\frac{2(4\alpha+5)}{(2\alpha+1)}+1\right]\times\frac{\sqrt{3(\alpha+2)(\alpha+3)}}{(2\alpha+1)}\varepsilon_{10}\ , \tag{17c}$$

$$\varepsilon_{30}=\frac{3}{(2\alpha+1)}\left[\frac{(\alpha+2)}{(2\alpha+1)}\right]^{1/2}\varepsilon_{10}\ , \tag{17d}$$

which, when we take

$$\lim_{\gamma\to\infty}\left[\frac{2\gamma}{\pi}\right]\varepsilon^i_{nm}\ ,$$

will reduce to the dipole matrix elements of the harmonic potential for which there is no overtone.

ABSORPTION COEFFICIENT

From the interaction matrix element of a sinusoidal perturbation already given, we can obtain the transition probability for pure translational transitions in terms of the effective moment, the field strength, and a normalized line-shape function, which accounts for broadening mechanisms such as lattice vibrations. The absorption cross section and the bulk absorption coefficient for a single transition at line center can be expressed in terms of the transition probability as

$$\alpha(\omega_{nm})=\sigma(\omega_{nm})f\rho=\frac{\hbar\omega\Gamma_{nm}}{I}f\rho=\frac{2|\mu^{\mathrm{eff}}_{nm}|^2}{\varepsilon_0 c\hbar}\left[\frac{\omega}{\Delta\omega}\right]f\rho\ , \tag{18}$$

where ρ is the density of cages, which for β-quinol is 2.29×10^{21} cm^{-3}, and f is the fraction of cages which are occupied.

For an argon clathrate at liquid helium temperature 1.2 K, only the 0 to 1 transition will contribute to the absorption, since $k_BT=0.8$ cm^{-1}. Using $\alpha=20.25$, and $\Omega=0.876$ cm^{-1}, and a linewidth of the 0 to 1 transition of 1.5 cm^{-1} (Ref. 13), an absorption coefficient of 42 cm^{-1} was obtained for unpolarized light with 100% cage occupation.

Although an absolute measure of the absorption coefficient of an argon clathrate is not presently available, published absorption spectra in arbitrary units indicate that the absorption coefficient of argon should be comparable to that of nitrogen, which is available.

Allen[41] has published transmission spectra of a powdered N_2 clathrate suspended in paraffin at 1.2 K. According to his data, the first rattling motion transition is at 54 cm^{-1}. The absorption line changes the transmittance through a 1.8 mm sample from a background value of approximately 0.78 to a value of 0.68. The paraffin clathrate suspension was 3.9% clathrate, while the clathrate had 81% of its cages filled. This gives an absorption coefficient for a pure clathrate sample with 100% filled cages of 24 cm^{-1}.

The rattling line measured by Allen, however, shows a linewidth of ~4 cm^{-1}, while the measurements taken by Burgiel *et al.* on single-crystal samples showed a linewidth of 2 cm^{-1}. This indicates that the grinding process used by Allen to powder his samples introduces a fair amount of inhomogeneous broadening, probably due to an inhomogeneous stress distribution in the microcrystals. Since the absorption coefficient is inversely proportional to the linewidth, the absorption coefficient for a single-crystal N_2 clathrate with all cages filled should be approximately 50 cm^{-1}, showing good agreement between theory and experiment.

THIRD-HARMONIC GENERATION

The presence of an inversion center indicates that the lowest order allowed nonlinear process will be a third-order process, such as third-harmonic generation. This can also be seen by examining the selection rules for translational transitions, which are determined by the factor ε_{mn}. Only parity violating transitions are forbidden, so there will be weak, but nonzero, overtone matrix elements for all odd transitions.

Direct measurement of an overtone absorption line would be extremely difficult at best, since absorption is proportional to the square of the dipole moment. For example, from Eq. (17d), the zero to three overtone transition in the argon clathrate is expected to be about 10^3 times weaker than the primary absorption line.

However, although the overtone matrix element is very weak, the fact that it is nonzero indicates that there will be a nonzero third-order susceptibility for third-harmonic generation. That is, there will be a nonzero cross section for the simultaneous absorption of three photons at ω and emission of one photon at 3ω. The susceptibility is derived by calculating the polarization of the medium, with the third harmonic susceptibility obtained from the component of the polarization oscillating at 3ω.

Due to the large linewidths of this system, coherent effects and saturation will be negligible, even for the highest available far-infrared pulse intensities; thus a first-order perturbation approach will suffice to calculate the susceptibility.

We start with the wave function

$$|\psi\rangle=\sum_{m=0}^{3}a_m e^{-i(\omega_0+m\omega)t}m\rangle\ , \tag{19}$$

where $|m\rangle$ now represents the wave function (9) in the atomic ground state, and the phase oscillation of the mth eigenstate is at the mth harmonic of the applied field plus the ground-state frequency. The polarization of the medium can be calculated from the expectation value of μ^{eff} from which the component that oscillates at 3ω is

$$P(3\omega)=2f\rho\,\text{Re}(\mu_{03}a_3e^{-i3\omega t})\ . \tag{20}$$

The third-harmonic polarization, therefore, depends only upon a_3, which we find to leading order to be

$$a_3=-\frac{iE^3\mu_{32}\mu_{21}\mu_{10}}{8\hbar^3\delta_3\delta_2\delta_1}\ , \tag{21}$$

where $\delta_m=\omega_m-\omega_0-m\omega$.

The third-harmonic susceptibility is defined in terms of the polarization component at 3ω as

$$P(3\omega)=\varepsilon_0\text{Re}(\chi^{(3)}_{3\omega}E^3_{\omega}e^{-i3\omega t})\ , \tag{22}$$

and therefore by comparison of Eqs. (10)–(22) we find

$$\chi^{(3)}_{3\omega}=\frac{f\rho\mu_{32}\mu_{21}\mu_{10}\mu_{03}}{4\varepsilon_0\hbar^3(\omega-\omega_{10}+i\tau_{10}^{-1})(2\omega-\omega_{20}+i\tau_{20}^{-1})(3\omega-\omega_{30}+i\tau_{30}^{-1})}\ , \tag{23}$$

where the imaginary contributions to the energy denominators have been added to account for the dephasing of the energy levels.

Assuming that the dephasing rates τ_{02} and τ_{03} are equal to τ_{01}, we plot in Fig. 2 the absolute magnitude of the susceptibility for an argon clathrate with 100% filled cages.

From the form of the susceptibility in Eq. (23) we see that there is a resonant enhancement at $\omega=\omega_{10}$, $\omega=\omega_{20}/2$, and $\omega=\omega_{30}/3$, so that the denominator will be minimized when all three conditions are satisfied. However, this condition can only be satisfied for the equally spaced energy levels of the harmonic oscillator, for which there are no overtone matrix elements. The susceptibility is a maximum when there is enough anharmonicity to produce an overtone matrix element, while still maintaining a degree of multiple resonance enhancement.

The clathrate system fulfills these requirements, making it a very good material for third-harmonic generation. The reason for this is that the transition linewidths are comparable to the $\omega_{21}-\omega_{10}$ and $\omega_{32}-\omega_{21}$ frequency shifts, so that there will be an overlap of he $\omega=\omega_{10}$ and the $\omega=\omega_{30}/3$ resonances a the $\omega=\omega_{20}/2$ resonance. Thus, even though the large linewidths will result in a relatively low peak for each resonance, the product of the three will be relatively large because of the resonance overlap. The peak of the susceptibility, which is near $\omega=\omega_{20}/2$, is 2.2×10^{-20} m^2/v^2, and corresponds to a microscopic susceptibility of 1×10^{-47} m^5/V^2 per atom.

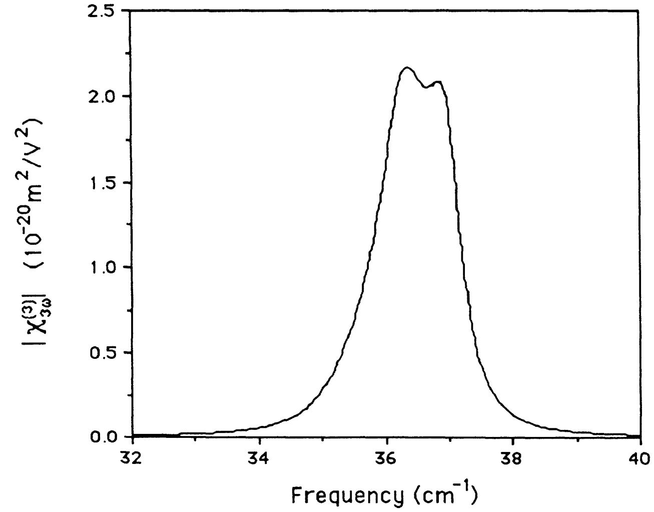

FIG. 2. Absolute magnitude of the susceptibility for an argon clathrate with 100% filled cages.

This value can be compared with the microscopic susceptibility for frequency tripling of infrared radiation by molecular vibrational transitions;[42,43] CO, for example, has a calculated value[44] of $7.7\times10^{-50}\text{m}^5/\text{V}^2$. These systems are also nearly harmonic, yet have relatively narrow linewidths, and complications due to the rovibrational structure.

In practice, the conversion efficiency of tripling infrared radiation in molecules is severely limited by the low saturation intensity, due to the narrow linewidths.[43] Thus the susceptibility will saturate due to single-photon absorption at the intensities necessary to generate the third harmonic. The clathrate system, on the other hand, will not saturate even for the highest possible FIR pulse intensities. This is another way in which the large linewidths are advantageous.

Thus we see that the clathrate system should be an efficient medium for the third harmonic generation. In summary, we have found that the important features of the motion of small enclathrated molecules responsible for optical activity are independent of the details of te potential symmetry, and can be effectively modeled with a symmetric O_h Pöschl-Teller potential. Based upon the success of this model in explaining the infrared activity of the rattling motion and prediction of the linear absorption coefficient, we have calculated the third-order susceptibility for third-harmonic generation and found that his should be an efficient material for frequency tripling in the far infrared.

In addition, it may be possible to generate bulk second-order nonlinear response from noncentrosymmetric systems such as β-quinol:CH_3H clathrates using their librational or rattling modes. This possibility is currently under investigation.

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