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STUDY OF DISPERSIVE RAMAN MODES IN Cu_2O BY RESONANT RAMAN SCATTERING

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ABSTRACT: We have observed shifts in energy of a number of Raman modes of Cu_2O as a function of incident photon energy. We explain such energy shifts as due to dispersion in the phonons involved and obtain quantitative agreement between theory and experiment. From our data we have also determined the effective mass of the 1s yellow exciton in Cu_2O to be $(3.0 \pm 0.2)\ m_o$.

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It is generally accepted[1] that one-phonon Raman modes are characterized by zone-center phonons while multiphonon Raman modes reflect the phonon density-of-states near critical points. In either case for a given crystal orientation, the Raman frequency shift is independent of the exciting photon energy. In this Letter we report for the first time the observation of some Raman modes in Cu_2O whose frequencies vary with the exciting laser frequency. We have developed a theory to explain our results quantitatively and shown that it is possible to obtain phonon dispersion and effective mass of the 1s exciton band in Cu_2O by resonance Raman scattering (RRS).

Recently Yu et al.[2] have shown that RRS of the $2\Gamma_{12}^-$-phonon mode in Cu_2O[3] is dominated by the scattering process shown in Figure 1(a). For a fixed incident photon energy ω_i, the momentum q of the Γ_{12}^- phonon emitted is determined uniquely by the resonance condition:

$$\omega_i = \omega_1 + \hbar q^2/2M + \omega_o(q) \qquad (1)$$

where ω_1 and ω_o are respectively the energies of the 1s yellow exciton at $q = 0$ and the Γ_{12}^- phonon and M is the effective mass of the 1s exciton band which is assumed to be spherical. Thus by measuring the energy of the $2\Gamma_{12}^-$ mode as a function of ω_i one can in principle measure the dispersion curve of the Γ_{12}^- phonon for q up to 2×10^7 cm^{-1} or about 1/4 of the B.Z. However no such shift in the energy of the $2\Gamma_{12}^-$ mode was observed. This is because the Γ_{12}^- mode happens to be almost dispersionless[4]. But there are other phonons in Cu_2O more dispersive than the Γ_{12}^- phonon. This prompted us to measure the position of other Raman peaks of Cu_2O as a function of ω_i. Our measurements were performed at $\sim$ 2°K using a conventional Raman spectrometer and a CW dye laser[5] on single crystals of Cu_2O grown by oxidation of pure copper and from melt. Results from both kinds of samples are essentially

identical. Samples grown from melt have much stronger luminescence background which tends to obscure the weaker Raman lines. We therefore presented here only results obtained from samples grown by oxidation of Cu. Figures 2(a) and (b) show two Raman spectra of Cu_2O obtained with two different ω_i. We notice that the peaks labelled Y and Z have clearly shifted in energy with ω_i.

In Figure 3 we have plotted the peak position of all the Raman modes of Cu_2O between 190 and 400 cm^{-1} as a function of ω_i. In this paper we shall consider only the modes X, Y, Z and $\Gamma_{12}^- + \Gamma_{15}^{-(1)}$ and leave the rest to a more detailed future publication.

RAMAN MODE: Y

We consider the peak Y first because of its comparatively larger cross-section. We notice in Figure 3 that this peak starts by splitting off from the $2\Gamma_{12}^-$ mode (220 cm^{-1}) and shifts to larger values of $\omega_i - \omega_s$ as ω_i increases above the phonon-assisted excitonic absorption edge ($\omega_1 + \omega_o$ = 16514 cm^{-1}). This suggests that this mode is due to scattering of two Γ_{12}^- phonons plus a low energy dispersive phonon which is presumably a longitudinal acoustic (LA) phonon [LA phonons couple more strongly to excitons than TA phonons]. There is also good reason to expect such an acoustic-phonon sideband of the $2\Gamma_{12}^-$ mode. In Reference 2 it was shown that the damping γ of the 1s yellow exciton with a non-zero momentum q is dominated by the damping γ_{ac} due to emission of an acoustic phonon. From the 'cascade' theory of Martin and Varma[6], we expect the ratio of the intensity of this sideband to the intensity of the $2\Gamma_{12}^-$ mode to be $\gamma_{ac}/\gamma \lesssim 1$.

The above interpretation is supported by the following quantitative analysis. Applying perturbation theory to the scattering process shown in Figure 1(b), we can show that the Raman cross-section of the $2\Gamma_{12}^- + LA\ (\omega_{ak})$

mode is given by:[7]

$$R_Y(\omega_i, \omega_i - \omega_s = 2\omega_o + \omega_{ak}) \propto \begin{cases} \alpha(\omega_i)\gamma_{ac}(q,k)\gamma^{-2}(q) & \text{for } 0 \leq k \leq 2(q - M\nu/\hbar) \\ 0 & \text{Otherwise} \end{cases} \quad (2)$$

where $\gamma_{ac}(q,k) \sim k^2[1 + 0(k^2)]/q$ is the damping of the 1s exciton with momentum q via emission of LA phonons with momentum k, $\omega_{ak} = \nu k$ is the LA phonon frequency, ν is the LA phonon velocity and α is the absorption constant. In order to compare Eq. (1) with the observed Raman spectra we neglect the $0(k^2)$ term in $\gamma_{ac}(q,k)$ and convolute R_Y with the slit function (which is a Gaussian with a half-width $(\ell n\ 2)\Delta = 2\ cm^{-1}$) of the spectrometer. The Raman spectrum is then given by:

$$I_Y(\omega_i, \delta\omega = \omega_i - \omega_s - 2\omega_o) \propto \int_0^{2\nu(q - M\nu/\hbar)} d\omega'(\omega')^2 \exp\left[-\left(\frac{\omega' - \delta\omega}{\Delta}\right)^2\right] \quad (3)$$

The dotted curves in the inserts of Figure 2 are calculated from Eq. (3) using $\nu = 4.15 \times 10^5$ cm/sec for the LA phonons in Cu_2O[8] and M as an adjustable parameter ($M = 2.9\ m_o$ and $3.2\ m_o$ for $\omega_i = 16570$ and $16587\ cm^{-1}$ respectively). The momentum q is determined by ω_i from Eq. (1). For all ω_i studied the calculated spectra fit quite well the experimental spectra with $M = (3.0 \pm 0.2)\ m_o$ except for small values of $\delta\omega$. This discrepancy tends to be bigger for larger ω_i and suggests that the $0(k^2)$ term is significant especially for large k. Using $M = 3.0\ m_o$ we have computed from Eq. (3) the peak position of the calculated Raman spectrum as a function of ω_i. The theoretical curve, shown as a solid line in Figure 3, reproduces the experimental peak positions quite well. It should be noted that for reasons which will not be discussed here the above value of M is a factor of 2 larger than the one deduced from magneto-optical absorption[9].

As a further check on our theory we have plotted in Figure 1(c) the peak Raman intensity of Y as a function of ω_i. The solid curve is a plot of Eq. (2) with $k = 2(q-M\nu/\hbar)$ and α and $\gamma(q)$ given by their expressions in Reference 2. In particular we have

$$\gamma \sim \begin{cases} A + (\omega_i-\omega_1-\omega_o) & \omega_1+\omega_o \leq \omega_i \leq \omega_1+3\omega_o \\ A + (\omega_i-\omega_1-\omega_o)+B(\omega_i-\omega_1-3\omega_o)^{1/2} & \omega_i \geq \omega_1+3\omega_o \end{cases} \quad (4)$$

For the solid curve in Figure 1(c) we have used $A = 45$ cm^{-1} and $B \sim 20$ cm^{-1}. They agree well with the values of $A \sim 39$ cm^{-1} and $B \sim 30$ cm^{-1} used to fit the experimental $2\Gamma_{12}^-$ data in Reference 2.

RAMAN MODE: Z

The change in the peak Z with ω_i is similar to the peak Y except for its weaker intensity. It is natural to interpret it as a $2\Gamma_{12}^-$ + 2LA mode.

The Raman cross-section in this case can be shown to be:

$$R_Z(\omega_i,\omega_i-\omega_s=2\omega_o+\omega_{ak_1}+\omega_{ak_2}) \propto \alpha(\omega_i)\gamma_{ac}(q,k_1)\gamma_{ac}(q,k_2)\gamma^{-3}(q) \quad (5)$$

for $0 \leq k_1 \leq 2(q - M\nu/\hbar)$ and $0 \leq k_2 \leq 2\sqrt{q^2-2M\nu k_1/\hbar} - 2M\nu/\hbar$ and zero otherwise. The Raman spectrum is given by:

$$I_Z(\delta\omega=\omega_i-\omega_s-2\omega_o) \propto \int_{\omega_{min}}^{\omega_{max}} d\omega'(\omega')^2(\delta\omega-\omega')^2 \quad (6)$$

with ω_{max} = minimum of $\delta\omega$ and $2\nu(q- M\nu/\hbar)$ and ω_{min} = maximum of 0 and $\delta\omega- 2M\nu^2/\hbar -2\nu\sqrt{q^2 -2M\delta\omega/\hbar}$. The peak position in the Raman spectrum can be calculated numerically from Eq. (6) as a function of ω_i. This is shown as the solid curve in Figure 3 using $M = 3.0\ m_o$ obtained from Y and no adjustable parameter. The excellent agreement with experiment lends further support to our theory. The corresponding calculated Raman spectra (with peak height normalized to experiment) for $\omega_i = 16570$ and 16587 cm^{-1} are shown as the

dashed curves in the inserts of Figure 2. Again reasonable agreement with experiment is found.

RAMAN MODES: X and Γ_{12}^{-} + $\Gamma_{15}^{-(1)}$

The very weak intensity of the peak X and its otherwise similarity in behavior to Y suggests that it is a $2\Gamma_{12}^{-}$ + TA mode. Using the same calculations as we did for the Y peak, but with a TA phonon velocity = $0.3v$ replacing v, we can predict well the peak position of the X mode as a function of ω_i, as shown by the solid curve in Figure 3. The TA phonon velocity obtained from the elastic constants[8] is $0.32v$. Unfortunately its weak intensity prevents further quantitative investigation.

Figure 3 also shows that the Γ_{12}^{-} + $\Gamma_{15}^{-(1)}$ mode has a linear splitting with ω_i. According to the phonon dispersion curves of Cu_2O calculated by Carabatos and Prevot[4], the frequency of the TO component of the $\Gamma_{15}^{-(1)}$ phonon decrease linearly while that of the LO component increase linearly with q^2. As the dispersion of the Γ_{12}^{-} phonon is negligible, it is obvious from Eq. (1) that the splitting of the Γ_{12}^{-} + $\Gamma_{15}^{-(1)}$ Raman mode should be proportional to $\omega_i-\omega_1-\omega_o$ as observed. At ω_i = 16864 cm^{-1} ($q \sim \frac{1}{4}$ B.Z. using M = 3.0 m_o) this TO-LO splitting was found experimentally to be 8 cm^{-1} while the theoretically predicted splitting is 9 cm^{-1}.

In conclusion we have demonstrated that using RRS it is possible to observe the dispersion of the acoustic and $\Gamma_{15}^{-(1)}$ optical phonons of Cu_2O from zone-center out to $\sim \frac{1}{4}$ B.Z. We have also determined the effective mass of the 1s yellow exciton band to be $(3.0 \pm 0.2)m_o$.

We wish to acknowledge helpful discussions with Drs. F. Stern and E. Burstein and expert technical assistance from J. Bradley. We are grateful to Prof. Y. Petroff for the Cu_2O samples used in this experiment.

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FIGURE CAPTIONS

Figure 1 Schematic representation of the RRS of (a) $2\Gamma_{12}^-$ phonons and (b) $2\Gamma_{12}^-$ + acoustic phonon with the 1s exciton as the intermediate state. Notations are ⟶ 1s yellow exciton; ⟹ β exciton; - - - - photon; ∿∿∿ Γ_{12}^- phonon and ≈≈≈ acoustic phonon. (c) Peak intensity of the Raman mode Y of Cu_2O as a function of incident photon energy ω_i. The solid curve is a theoretical curve obtained from Eq. (2) [see text].

Figure 2 Raman spectra of Cu_2O for two different incident photon energies: (a) 16587 cm^{-1} and (b) 16570 cm^{-1}. The inserts show the Raman modes Y and Z after removal of the luminescence background. The dotted and dashed curves are theoretical curves [see text].

Figure 3 The position of all the observed Raman modes of Cu_2O between 190-400 cm^{-1} as a function of incident photon energy. The broken curves are drawn for clarity. The solid curves are theoretical curves discussed in the text. The vertical bars over the experimental points indicate the half-widths of the corresponding Raman peaks.

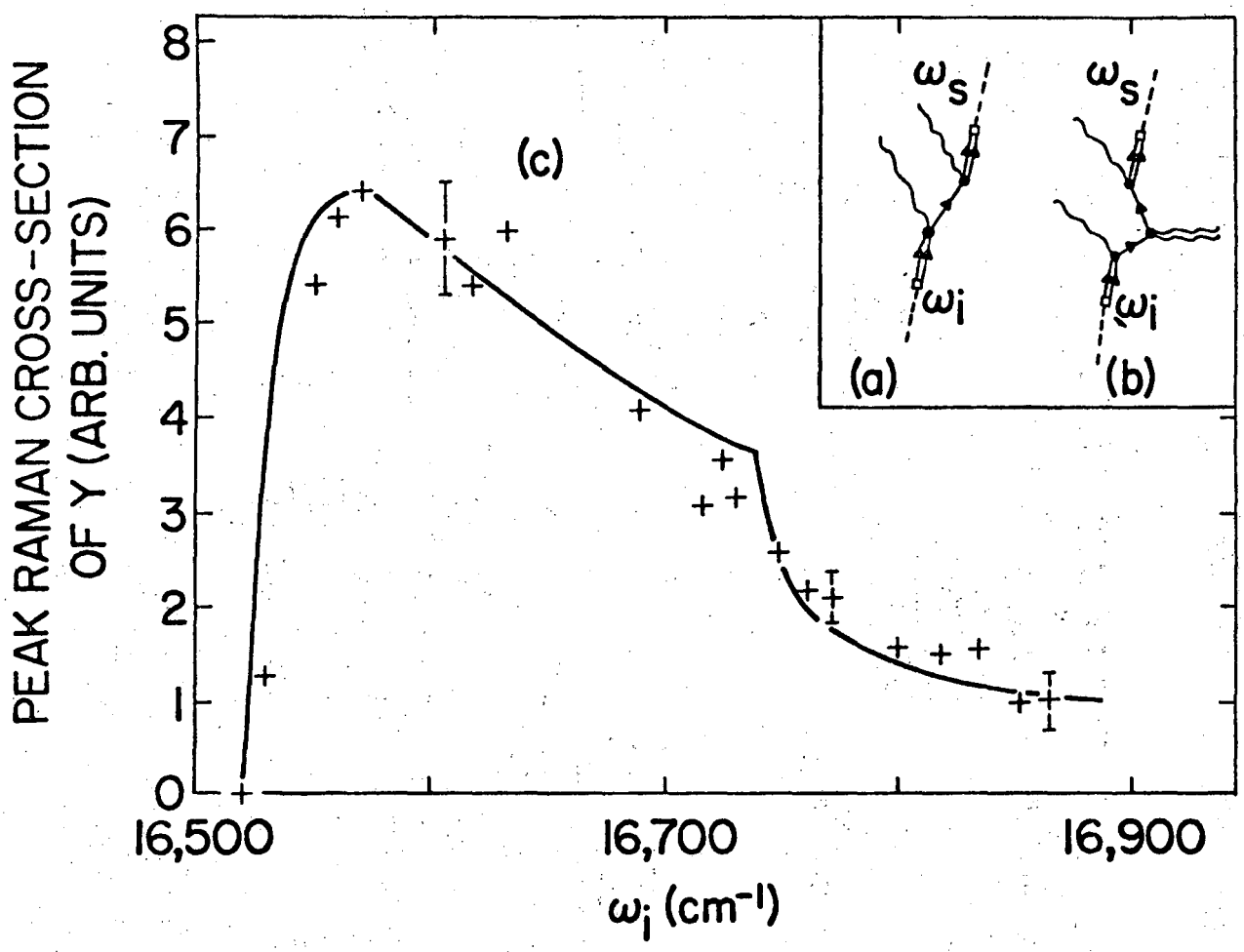
PEAK RAMAN CROSS-SECTION OF Y (ARB. UNITS)
0
1
2
3
4
5
6
7
8
16,500
16,700
16,900
ω_i (cm^{-1})
(c)
ω_s
ω_i
(a)
ω_s
ω_i
(b)

Fig. 1

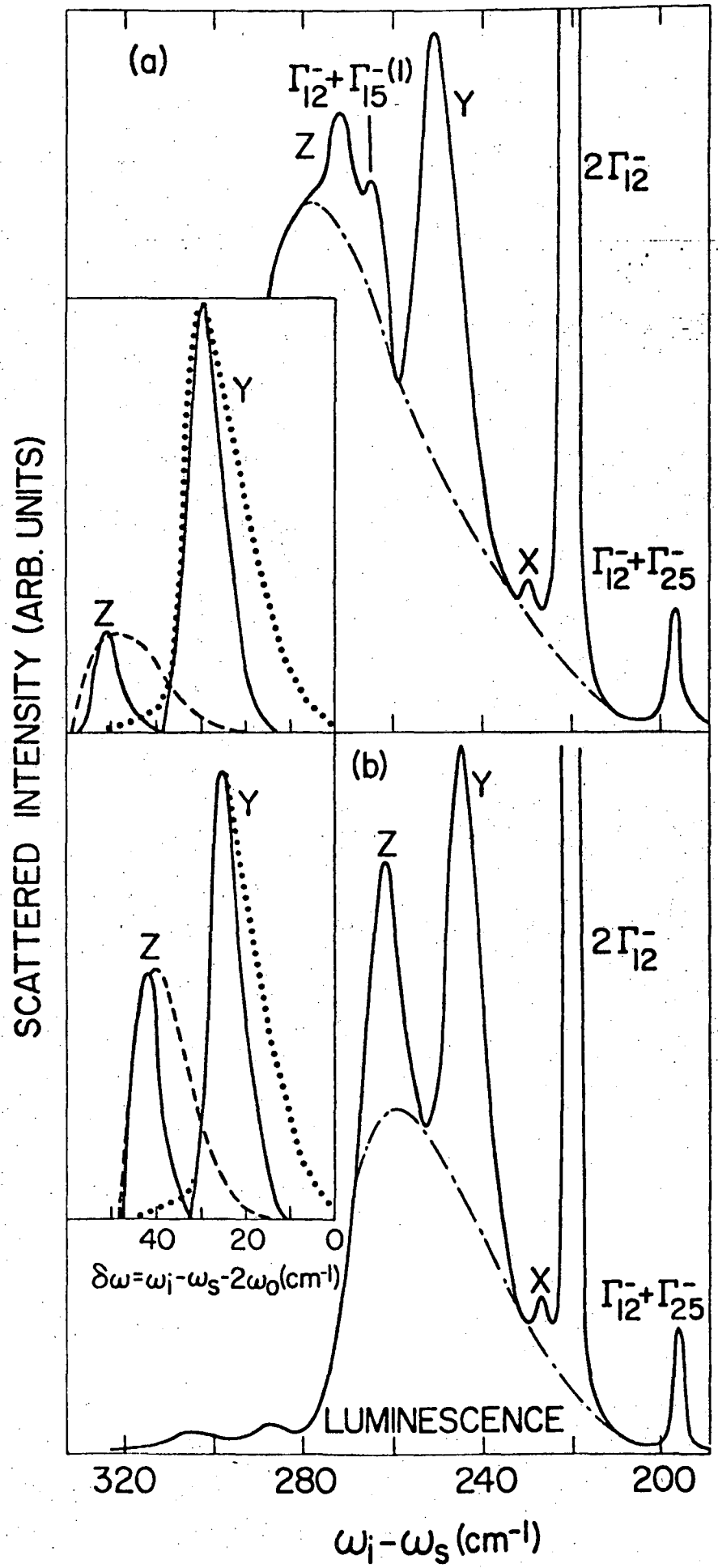
(a)
$\Gamma_{12}^- + \Gamma_{15}^-(1)$
Z
Y
$2\Gamma_{12}^-$
X
$\Gamma_{12}^- + \Gamma_{25}^-$
Y
Z
(b)
Y
Z
$2\Gamma_{12}^-$
X
$\Gamma_{12}^- + \Gamma_{25}^-$
LUMINESCENCE
40
20
0
$\delta\omega = \omega_i - \omega_s - 2\omega_0 (cm^{-1})$
SCATTERED INTENSITY (ARB. UNITS)
320
280
240
200
$\omega_i - \omega_s (cm^{-1})$

Fig. 2

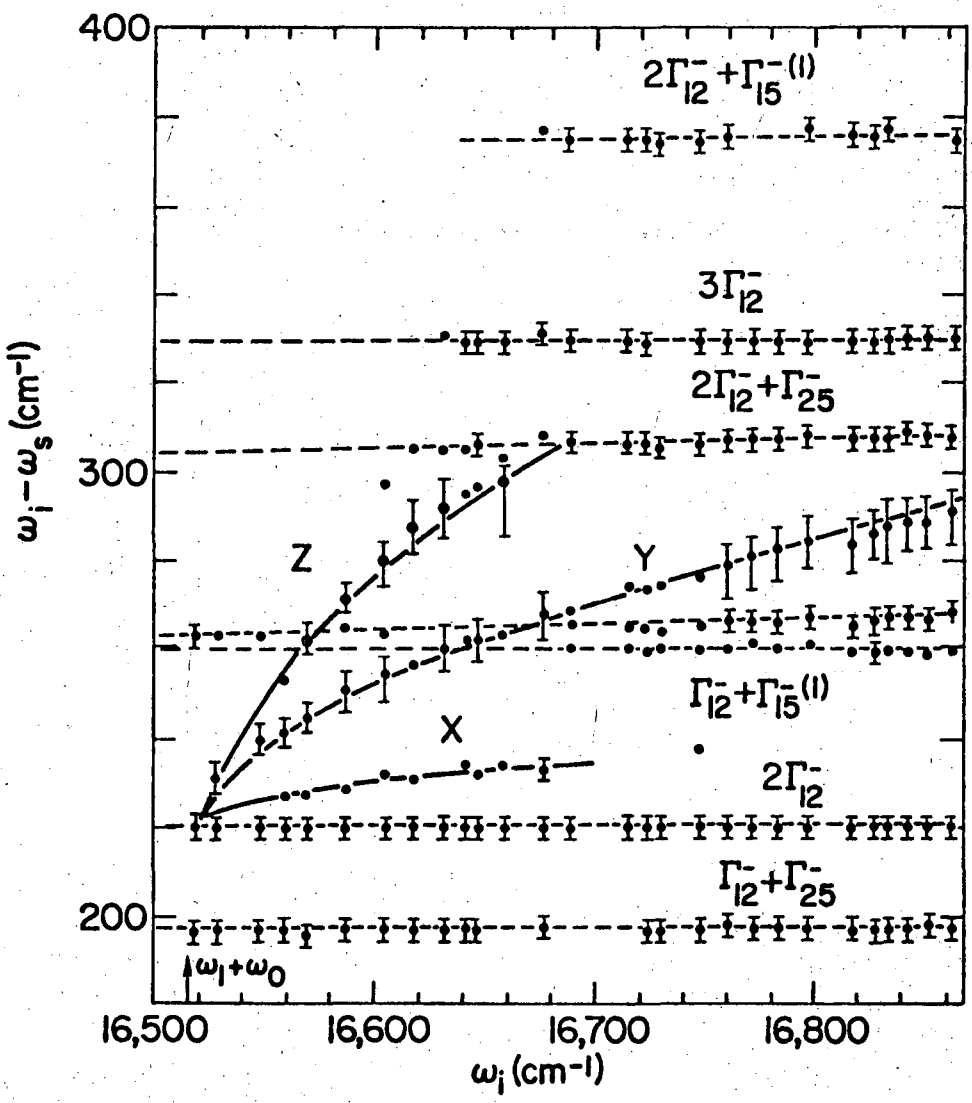
400
300
200
$\omega_i - \omega_s$ (cm^{-1})
$2\Gamma_{12}^- + \Gamma_{15}^{-(1)}$
$3\Gamma_{12}^-$
$2\Gamma_{12}^- + \Gamma_{25}^-$
Z
Y
X
$\Gamma_{12}^- + \Gamma_{15}^{-(1)}$
$2\Gamma_{12}^-$
$\Gamma_{12}^- + \Gamma_{25}^-$
$\omega_1 + \omega_0$
16,500
16,600
16,700
16,800
ω_i (cm^{-1})

Fig. 3

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