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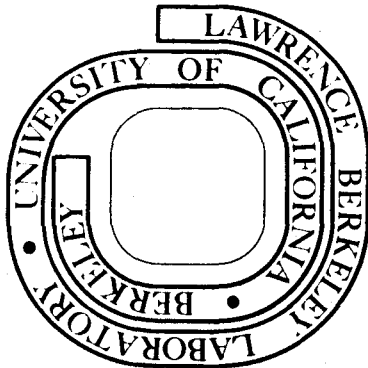
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MULTIPLE RESONANCE EFFECTS IN RAMAN SCATTERING

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November 1973

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## Multiple Resonance Effects in Raman Scattering

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## ABSTRACT

We have observed sharp resonance enhancements in some two-phonon Raman modes of  $\text{Cu}_2\text{O}$  around the  $n = 2$  to 6 peaks of the yellow exciton series. We explain the results quantitatively by a theory which allows for multiple resonances in the scattering process. Possible multiple resonance effects in the resonant Raman scattering in  $\text{BiI}_3$  and  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$  are also discussed.

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It is well known that the Raman tensor obtained from the perturbation theory can be written as a sum of terms of the form:<sup>1,2</sup>

$$\frac{M}{(\omega_l \pm \omega_1)(\omega_l \pm \omega_2) \dots (\omega_l \pm \omega_n)} \quad (1)$$

where M stands for the product of matrix elements,  $\omega_l$  is the incident photon energy and  $\omega_1, \dots, \omega_n$  contain phonon energies and energies of the intermediate states involved.  $n-1$  is the order of the Raman process. So far, most work on resonance Raman scattering (RRS) has considered only cases where one of the energy terms in the denominator of Eq. (1) vanishes.<sup>1-4</sup> Intuitively, one would expect the enhancement in the Raman tensor to be even stronger when two or more energy terms in Eq. (1) vanish simultaneously. We will refer to such cases as multiple resonances and in particular, a double resonance occurs when two energy terms vanish simultaneously. Although double resonance has been proposed<sup>5</sup> to explain the energy shift of the RRS peak from the optical  $E_1$  peak in InSb, it has not been positively identified. To our knowledge, no unambiguous case of multiple resonance effects (MRE) has yet been reported. In this letter, we show how MRE can account quantitatively for the sharp resonance enhancements we have observed in several two-phonon Raman modes of  $\text{Cu}_2\text{O}$  at its yellow exciton series ( $n = 2, 3, \dots, 6$ ). This is the first time RRS at excited states of an exciton with  $n$  as large as 6 has been observed. Other possible examples of MRE in  $\text{BiI}_3$ , CdS and  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$  will also be discussed.

Before presenting our results on  $\text{Cu}_2\text{O}$ , we give first a summary of its physical properties.<sup>6</sup> Because of inversion symmetry, all electronic and vibrational states of  $\text{Cu}_2\text{O}$  have definite parity.<sup>7</sup> The energy and

symmetry of its zone center phonons have been established by a combination of photoluminescence,<sup>8</sup> infrared<sup>9</sup> and resonant Raman studies:<sup>10,11</sup>  $\Gamma_{25}^-$  (88  $\text{cm}^{-1}$ ),  $\Gamma_{12}^-$  (110  $\text{cm}^{-1}$ ),  $\Gamma_{15}^{-(1)}$  (TO - 149  $\text{cm}^{-1}$ , LO - 153  $\text{cm}^{-1}$ ),  $\Gamma_2^-$  (348  $\text{cm}^{-1}$ ,  $\Gamma_{25}^+$  (515  $\text{cm}^{-1}$ ), and  $\Gamma_{15}^{-(2)}$  (TO - 640  $\text{cm}^{-1}$  and LO - 660  $\text{cm}^{-1}$ ). The yellow exciton series of  $\text{Cu}_2\text{O}$  shows up in the absorption spectrum (see Figure 1a) as a series of sharp, asymmetric peaks obeying the Rydberg Equation:<sup>6</sup>

$$\omega_{\text{no}} = 17,525 - \frac{786}{n^2} \text{ cm}^{-1} \quad (n = 2,3,4,5). \quad (2)$$

The 1s exciton (16,399.5  $\text{cm}^{-1}$ ) is electric-dipole forbidden by selection rule.<sup>7</sup>

$\text{Cu}_2\text{O}$  has been unique in that its RRS results at the 1s yellow exciton<sup>10</sup> and the phonon-assisted absorption edge<sup>11</sup> are well understood and have contributed substantially towards the identification of the observed Raman modes. For example, all the odd parity zone center phonons showed strong resonance at the 1s exciton while two-phonon Raman modes (in which both phonons are odd and one is the  $\Gamma_{12}^-$  mode) showed enhancement at the absorption edge. In addition, we have now observed strong and sharp resonances in several two-phonon modes (involving at least one LO phonon) at the 2p, 3p, ..., 6p peaks of the yellow exciton. Our RRS results on  $\text{Cu}_2\text{O}$  was obtained at  $\sim 10^\circ\text{K}$  with a conventional Raman spectrometer and a CW dye laser tunable between 16000 and 18100  $\text{cm}^{-1}$ .

Figure 1 (b) shows the variation of the Raman cross-section of the 770  $\text{cm}^{-1}$   $\Gamma_{12}^- + \Gamma_{15}^{-(2)}$  (LO) two-phonon mode for  $\omega_{\text{q}}$  in the region of the yellow excitonic series. This was the only mode which showed strong resonances in this region.

To explain these results we have calculated the Raman cross-section  $R$  by perturbation theory. Among the many possible scattering processes, the one shown in Figure 1 (c) appears to be dominant since it gives the maximum number of resonances (i.e., two) and the strongest exciton-phonon coupling. The Raman cross-section, assuming the phonons involved are dispersionless,<sup>12</sup> can be approximated by:

$$R(\omega_\ell) \propto \sum_q \left| \sum_n \frac{M_{g,\beta_0} V_{\beta_0,1\vec{q}}^{(12)} V_{1\vec{q},n_0}^{(15)} M_{n_0,g}}{(\omega_\beta - \omega_s)(\omega_{1\vec{q}} - \omega_\ell + \omega(\Gamma_{15}^{-(2)}))(\omega_{n_0} - \omega_\ell)} \right|^2 \quad (3)$$

where  $M$ ,  $V^{(12)}$ , and  $V^{(15)}$  denote the exciton-photon, exciton- $\Gamma_{12}$  phonon and exciton- $\Gamma_{15}^{-(2)}$  phonon interactions respectively, and the subscripts represent the various electronic states shown in Figure 1 (c). In Eq. (3) we have neglected the non-resonant background contribution.

It has been shown that<sup>11</sup>

$$\frac{M_{g,\beta_0} V_{\beta_0,1\vec{q}}^{(12)}}{\omega_\beta - \omega_s}$$

can be approximated by a constant and

$$\frac{1}{|\omega_{1\vec{q}} - \omega|^2} \approx \frac{\delta(\omega_{10} + \frac{q^2}{2\mu} - \omega)\pi}{\gamma_1(\vec{q})} \quad (4)$$

where  $\gamma_1$  is the damping constant of the 1s exciton with wave vector  $\vec{q}$ .

Using these results, we can reduce Eq. (3) to

$$R(\omega_\ell) \propto \frac{1/2}{\gamma(x)} \left| \sum_n \frac{f_n(x) M_{n_0,g}}{\omega_{n_0} - \omega_\ell} \right|^2 \quad (5)$$

where  $x = \omega_{10} - \omega_\ell + \omega(\Gamma_{15}^{-(2)})$  and  $f_n(x)$  comes from the frequency dependence of  $V_{1\vec{q},n_0}^{(15)}$ . When  $\omega_\ell$  varies over only a narrow region around  $\omega_{n_0}$ , the dispersion of  $x^{1/2} f_n(x) / \gamma(x)$  can be neglected. Taking into account the damping  $\gamma_n$  of the nth exciton state and neglect overlap of adjacent



exciton peaks, we obtain for  $\omega_\ell \approx \omega_{no}$

$$R(\omega_\ell) = \frac{A_n}{\gamma_n} \alpha_n(\omega_\ell) \quad (6)$$

where  $\alpha_n(\omega_\ell)$  is the absorption coefficient of the  $n$ th exciton peak in the yellow series and  $A_n$  is nearly independent of  $\omega_\ell$ . Figure 1 (a) shows the absorption spectrum of an  $\text{Cu}_2\text{O}$  sample. It agrees well with previous measurements.<sup>6,13</sup> We obtain  $\alpha_n(\omega_\ell)$  by simply removing the background absorption due to phonon-assisted transitions in the same way as done by Nikitine et al.<sup>14</sup> The dependence of  $A_n$  on  $n$  can be calculated using the hydrogenic wave functions and assuming  $V^{(15)}$  to be given by the Fröhlich interaction.<sup>2</sup>  $\gamma_n$  is estimated from the experimental linewidth of  $\alpha_n$ .  $R(\omega_\ell)$  thus obtained is plotted as the solid curve in Figure 1 (b) with only one normalization constant. It is seen that agreement with experiment is fairly good. Part of the discrepancy in the fit is due to (1) uncertainty in the background absorption and (2) neglect of overlap of neighboring exciton peaks for  $n \geq 4$ .

Based on Figure 1 (c) it is possible to understand the absence of resonance enhancement in the other two-phonon modes. It is known that LO phonons couple strongly to excitons via the Fröhlich interaction and in  $\text{Cu}_2\text{O}$  only  $\Gamma_{12}^-$  couples the yellow exciton strongly to the  $\beta$ (allowed) excitons. Of the two possible LO phonons;  $\Gamma_{15}^{-(2)}$  has a much stronger dipole moment<sup>9,15</sup> and its energy more closely matches the separation the 1s exciton from the higher exciton states than  $\Gamma_{15}^{-(1)}$ . It should be pointed out that the strong resonant interband coupling between the 1s and 2p exciton states via the  $\Gamma_{15}^{-(2)}$  (LO) phonon can probably explain the large linewidth of the 2p exciton peaks.<sup>16</sup>

Although the  $\Gamma_{12}^- + \Gamma_{15}^{-(2)}$  (LO) mode was the only one to show clear enhancement at the yellow exciton series, we found that two other two-phonon modes  $2\Gamma_{15}^{-(1)}$  (LO) ( $308 \text{ cm}^{-1}$ ) and  $\Gamma_{15}^{-(1)}$  (LO) +  $\Gamma_{12}^-$  ( $264 \text{ cm}^{-1}$ ), in addition to the  $\Gamma_{12}^- + \Gamma_{15}^{-(2)}$  (LO) mode, showed strong enhancement when their scattered photon frequencies  $\omega_s$  were resonant with the yellow exciton series. (We did not study the  $2\Gamma_{15}^{-(2)}$  (LO) mode because the required  $\omega_q$  is outside the tuning range of our dye laser.) The dependence of their Raman cross-sections on  $\omega_s$  is shown in Fig. 2(a). Again, detailed considerations led us to conclude that the dominant contributions to the strong enhancements we observed come from MRE (in this case, triple resonances).

As an example, we consider the  $2\Gamma_{15}^{-(1)}$  (LO) mode since all the exciton-phonon matrix elements can be calculated in this case. For  $\omega_s$  in resonance with the 2p exciton, the dominant scattering process is that shown in Figure 2(b). Again using perturbation theory, we obtain the Raman cross-section for  $\omega_s \sim \omega_{20}$  as:

$$R(\omega_q) \approx 0 \text{ for } \omega_q - \omega(\Gamma_{15}^{-(1)}) - \omega_{30} < 0 \text{ and} \quad (7)$$

$$\propto (\omega_q - \omega(\Gamma_{15}^{-(1)}) - \omega_{30})^{1/2} \alpha(\omega_s) / \gamma_3 \gamma_2 \text{ otherwise.}$$

Similar expressions are obtained for  $\omega_s$  in resonance with the higher excitons. The theoretical results are shown as solid curves in Fig. 2(a) where the peak heights have been normalized to the experiment. Again there is good agreement between theory and experiment. Note that the resonance of  $\omega_q - \omega(\Gamma_{15}^{-(1)})$  with the  $n=3$  exciton states gave rise to the  $(\omega_q - \omega(\Gamma_{15}^{-(1)}) - \omega_{30})^{1/2}$  term in Eq. (7). The fact that Eq. (7) can reproduce the sharp drop in the experimental  $R(\omega_q)$  at  $\omega_q - \omega(\Gamma_{15}^{-(1)}) - \omega_{30} = 0$  gives strong support to our theory. The details of our theoretical calculations will appear in a later publication.

We also note that the  $308 \text{ cm}^{-1}$  mode has been observed in photo-

luminescence<sup>8</sup> and RRS of  $\text{Cu}_2\text{O}$  in the region of the blue and indigo excitons.<sup>17</sup> However, these measurements were not capable of determining whether this mode is a  $2\Gamma_{15}^{-(1)}$  or  $2\Gamma_{12}^- + \Gamma_{25}^-$  mode. Our result now shows that the  $308 \text{ cm}^{-1}$  Raman line is definitely a  $2\Gamma_{15}^{-(1)}$  (LO) mode.

Examples of MRE can also be found in  $\text{BiI}_3$  which is a layer semiconductor.<sup>18</sup> Recently, Gross et al.<sup>19</sup> have observed in the absorption spectrum of  $\text{BiI}_3$  a series of sharp lines purely electronic in character.<sup>20</sup> Petroff et al.<sup>20</sup> measured the enhancement of several Raman modes of  $\text{BiI}_3$  in the region of these discrete lines and the absorption edge. They found that a number of Raman lines exhibit sharp resonances when  $\omega_q$  is inside the absorption continuum but  $\omega_s$  is at resonance with these discrete lines. These sharp resonances are apparently due to double resonance since no enhancement was observed when  $\omega_q$  alone is at resonance with the discrete lines.

After surveying the literature we found other cases where MRE could be important in determining the RRS but lack of more complete data did not allow us to make quantitative comparisons between theory and experiment. Gross et al.<sup>21</sup> have measured RRS in  $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ . They found that the Raman cross-section of the  $n - \text{LO}$  ( $n = 1, 2, 3$  and  $4$ ) mode peaks whenever  $\omega_s$  was at resonance with the exciton whereas the  $3\text{LO}$  and  $4\text{LO}$  phonons showed no enhancement when  $\omega_q$  was at resonance. Similar results have also been observed in  $\text{CdS}$  by Leite et al.<sup>22</sup> and Klein et al.<sup>23</sup> Martin and Varma<sup>23</sup> have explained this phenomenon in terms of a "cascade" theory of hot luminescences, but we can also consider these cases as examples of MRE in RRS. The distinction between RRS and hot luminescence has been recently elucidated by Shen.<sup>24</sup>

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## FIGURE CAPTIONS

- Figure 1 (a) The absorption spectrum of  $\text{Cu}_2\text{O}$  measured at  $\sim 5^\circ\text{K}$ . The dotted curve represents the background absorption due to phonon-assisted transitions.
- (b) The Raman cross-section of the  $\Gamma_{15}^{-(2)}$  (LO) +  $\Gamma_{12}^-$  ( $770 \text{ cm}^{-1}$ ) mode of  $\text{Cu}_2\text{O}$  obtained at  $\sim 10^\circ\text{K}$  as a function of incident photon energies. The solid curve is the theoretical curve (Eq. (6)).
- (c) A schematic diagram of the dominant resonant Raman process at  $\omega_l \sim \omega_{30}$ . g stands for the ground state and  $\beta$  an allowed exciton.
- Figure 2 (a) The Raman cross-section of 3 two-phonon modes of  $\text{Cu}_2\text{O}$  measured at  $\sim 10^\circ\text{K}$  as a function of the scattered phonon energy  $\bullet\bullet 2\Gamma_{15}^{-(1)}$  (LO) ( $308 \text{ cm}^{-1}$ );  $\circ\circ \Gamma_{12}^- + \Gamma_{15}^{-(1)}$  (LO) ( $264 \text{ cm}^{-1}$ ) and  $++ \Gamma_{12}^- + \Gamma_{15}^{-(2)}$  (LO) ( $770 \text{ cm}^{-1}$ ). The solid curve is the theoretical curve.
- (b) A schematic representation of the Raman process responsible for the observed enhancement in the  $2\Gamma_{15}^{-(1)}$  (10) mode at  $\omega_s \sim \omega_{20}$ .

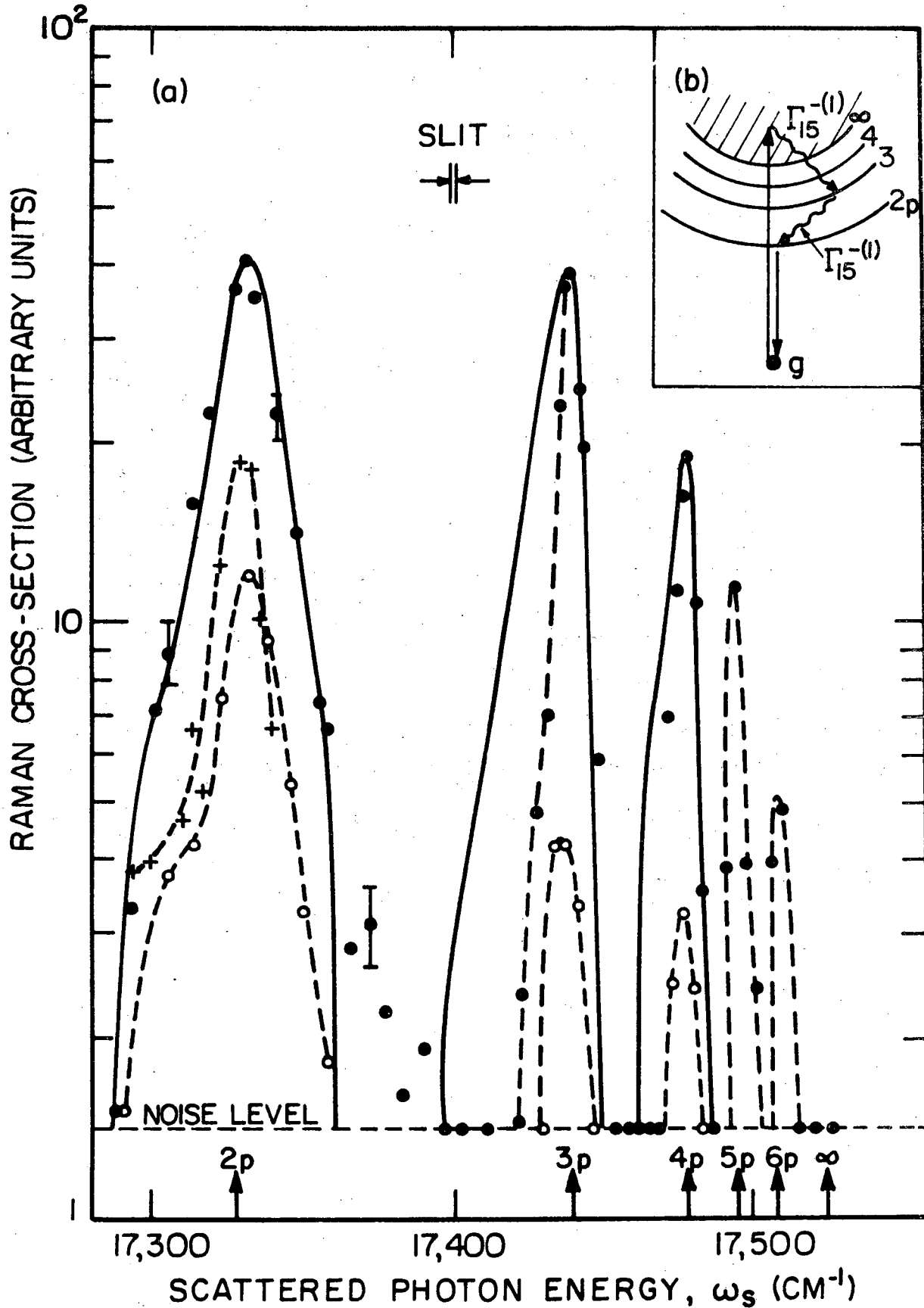
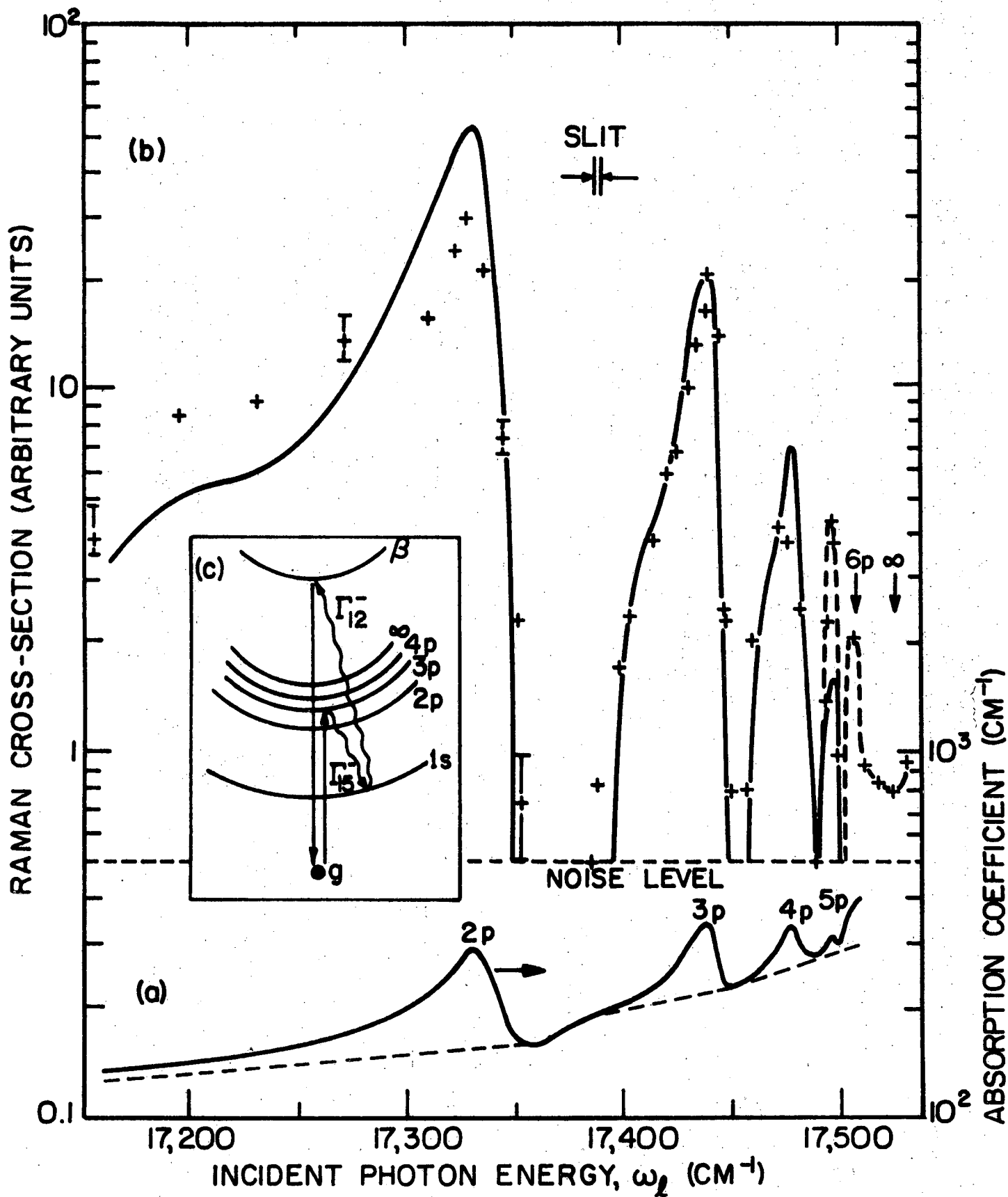


Fig. 2

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Fig. 1

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