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<sup>7</sup>P. K. Iyengar, G. Venkataraman, P. R. Vijayaraghavan, and A. P. Roy, Lattice Dynamics. Proceedings of the International Conference held at Copenhagen, Denmark, August 5-9, 1963, edited by R. F. Wallis (Pergamon Press, New York, 1965), p. 223. See also G. W. Lehman, T. Wolfram, and R. E. DeWames, *ibid.*, p. 101.

<sup>8</sup>R. E. DeWames, T. Wolfram, and G. W. Lehman, Phys. Rev. **138**, A717, (1965). The nonzero values of the atomic force constants for Mg [cf. Appendix A] were taken as  $\delta_1 = 0.0844$ ,  $\epsilon_{1x} = \epsilon_{1z} = 0.0525$ ,  $\alpha_2 = 1.0330$ ,  $\beta_{2x} = \beta_{2z} = 0.0507$ ,  $\delta_3 = 0.0057$ , and  $\epsilon_{3x} = \epsilon_{3z} = -0.0845$  in units of  $10^4$  dyne/cm.

<sup>9</sup>P. L. Smith, Phil. Mag. **46**, 744 (1955).

<sup>10</sup>R. S. Craig, C. A. Krier, C. W. Koffer, E. A. Bates, and W. E. Wallace, J. Am. Chem. Soc. **76**, 238 (1954).

<sup>11</sup>Finite concentration effects on  $C_p$  have been consid-

ered by Maradudin. See Ref. 1.

<sup>12</sup>Our statement to the contrary in a recent abstract [W. V. Johnston and J. A. Cape, Bull. Am. Phys. Soc. **11**, 47 (1966)] was fostered by an analytical error in the concentration of one of the alloys. What was labeled 1.0% was actually 0.7%.

<sup>13</sup>G. Kh. Panova and B. N. Samoïlov, Zh. Eksperim. i Teor. Fiz. **49**, 456 (1965) [translation: Soviet Phys. -JETP **22**, 320 (1966)].

<sup>14</sup>One expects that heavy-impurity localized modes should be manifest in other ways. Some evidence for localized modes in Be may be inferred from the recent measurements of Ahlers [G. Ahlers, Bull. Am. Phys. Soc. **10**, 1103 (1965); Phys. Rev. **145**, 419 (1966)], who has found that the specific heat of Be is extremely sensitive to purity. At low temperatures larger values of  $C_p$  are found for the less pure Be than for the purest specimens.

## TWO-PHOTON SPECTROSCOPY IN ANTHRACENE\*†

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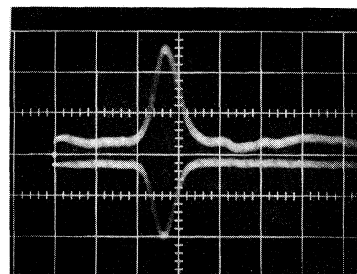
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(Received 21 April 1966)

Following the first observation of two-photon absorption by two red ruby photons in anthracene single crystals<sup>1,2</sup> a lively debate has developed about the nature of the transition and the type of excited state involved. Assuming that the observed effect was due to a second-order dipolar transition it was suggested that (1) an electronic state of even parity<sup>2</sup> or (2) a vibronic state of even parity<sup>3,4</sup> existed in the region of photon energies of twice the ruby-laser photon energy. Alternatively it was proposed<sup>5</sup> that the effect was caused by the  $(\vec{A} \cdot \vec{A})$  interaction term of the Hamiltonian. Proposals and measurements performed<sup>3-9</sup> to settle these questions have all concentrated on the behavior of the absorption of two laser photons.

We would like to report results of a different experimental approach to the problem, namely, that of two-photon spectroscopy.<sup>10</sup> A Nd laser source used in combination with a flash-tube source of variable photon energy allowed one to investigate the two-photon spectrum from 3.20 to 4.25 eV by directly measuring the absorption of light of the variable source during the laser burst. Figure 1 shows the coincidence of the two-photon absorption signal with the laser pulse. As shown, a particularly good signal-to-noise ratio was achieved through a setup improved over previously used apparatus.<sup>11</sup> Important changes in the earlier appa-

ratus include the following: (a) An additional monochromator was placed between the high-intensity flash tube (variable source) and the sample to avoid a population of the triplet state of the anthracene; (b) the intensity of the flash tube output was greatly enhanced by decreasing the pulse duration from 1 msec to 50  $\mu$ sec, a delay line being used to assure the proper timing of the laser pulse with the maximum output of the flash-tube pulse; (c) the plane of polarization of the laser source could be turned by 90° using a crystalline quartz rotor;



< 0.5  $\mu$  sec >

Time →

FIG. 1. Coincidence of the laser signal (lower trace) and the two-photon absorption signal (upper trace). Absorption gives rise to an upward signal on the oscilloscope.

(d) a Nd laser was used to avoid two-photon absorption by two laser photons and subsequent emission of blue light.

Typical results<sup>12,13</sup> are shown in Fig. 2. The two different vibronic spectra, type I and type II, were also obtained for a variety of other polarization combinations and crystal orientations and for crystals from different suppliers. In all cases type-I spectra were observed only if the light from the variable source was polarized parallel to the crystal *b* axis and type-II spectra only if polarized perpendicular to the *b* axis. Different polarization of the laser light with respect to the crystal axes gave identical spectra with about the same strength.

For an incident photon flux of  $N_L = 5 \times 10^{25}$  laser photons/cm<sup>2</sup> sec, the observed effect is of the order of 10% transmission change (at 3.85 eV) for a 2.5-cm long crystal. We calculate an absorption constant  $K = 4 \times 10^{-2}$  cm<sup>-1</sup>

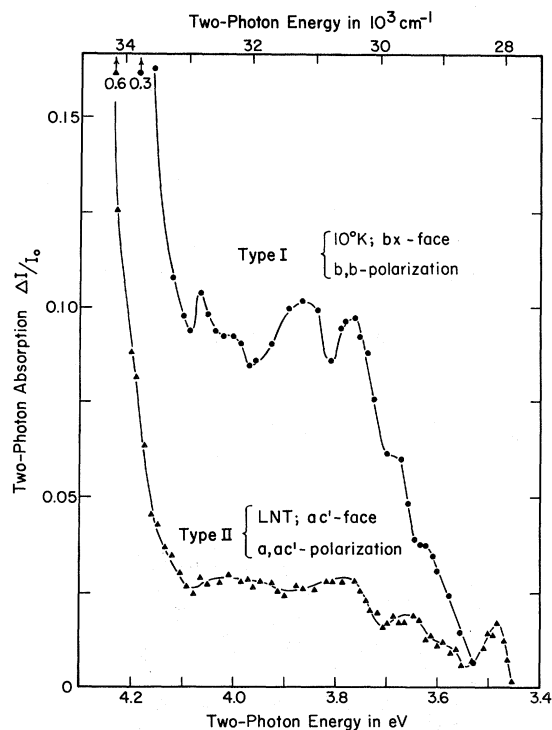


FIG. 2. Two-photon spectrum of anthracene single crystals. The relative change in transmission  $\Delta I/I_0$  of the light from a source of variable photon energy is plotted versus the combined photon energy of both sources. For the type-I spectrum the laser light and the light from the variable source were both polarized along the crystal *b* axis. For the type-II spectrum the laser light was polarized along the crystal *a* axis; the light from the variable source was unpolarized in a plane perpendicular to the crystal *b* axis.

and an absorption cross section of  $\sigma = 10^{-23}$  cm<sup>2</sup>. Dividing by the laser flux we get  $\sigma/N_L = 2 \times 10^{-49}$  cm<sup>4</sup> sec/photon and  $K/N_L = 8 \times 10^{-28}$  cm sec/photon. These values are in agreement with those reported by Hall, Jennings, and McClintock,<sup>14</sup> Hasegawa and Yoshimura,<sup>15</sup> and Weisz et al.,<sup>16</sup> if one considers the different energy position (3.56 eV) and the different size of the resonant denominator<sup>17,18</sup> for the absorption of two red ruby photons. Absorption of two Raman-shifted laser photons was also reported<sup>3</sup> at 3.18 eV. We did not find two-photon absorption in the region of 2.3-3.45 eV; the signal-to-noise ratio in this region is poor, however.

The steep rise of the effect towards higher photon energies is interpreted as being due to a dominant resonance denominator  $(E_{GI} - h\nu_v)^2$  which appears in second-order dipolar transitions<sup>17,18</sup> involving the  $(\vec{p} \cdot \vec{A})$  term of the interaction Hamiltonian.  $E_{GI}$  is the energy difference between an intermediate state *I* and a ground state *G* and  $h\nu_v$  is the energy of photons from the variable light source. This interpretation is favored by the fact that values of  $E_{GI}$  extrapolated from the results fall into the known, lowest odd-parity absorption bands of  $A_u$  and  $B_u$  symmetry around 25300 cm<sup>-1</sup> (3.13 eV) above the ground state.<sup>19-22</sup> Taken together with the experimental evidence of the dependence of the effect on the polarization of the variable light source, these facts suggest that an electronic intermediate level of  $A_u$  symmetry at 25213 cm<sup>-1</sup> (3.1255 eV) for type-I spectra<sup>19</sup> and an intermediate level of  $B_u$  symmetry at 25432 cm<sup>-1</sup> (3.1526 eV) for type-II spectra<sup>19</sup> contribute mainly to the observed effect.<sup>23</sup> In order to isolate the vibronic structure we multiplied the absorption constant  $K$  (calculated from the results of Fig. 2) by a factor  $F = \alpha(E_{GI} - h\nu_v)^2/h\nu_v$ , where  $\alpha$  is an arbitrary constant. The resultant vibronic structure, shown in Fig. 3, can be tentatively assigned to well-known  $a_g$  modes<sup>19-22</sup> of 350 cm<sup>-1</sup>, 1410 cm<sup>-1</sup>, 1170 cm<sup>-1</sup>, and combinations thereof.

We suggest then the existence of two different final states of even parity located at 3.48 and 3.58 eV, respectively, of mixed  $A_g$  and  $B_g$  symmetry. These final states might be even-parity electronic states in agreement with lowest two calculated<sup>24</sup> levels of  $B_{1g}$  and  $A_{1g}$  symmetry<sup>25</sup> in the molecule, which would both split into  $A_g$  and  $B_g$  sublevels in the crystal. Their calculated positions<sup>24</sup> in the molecule are around

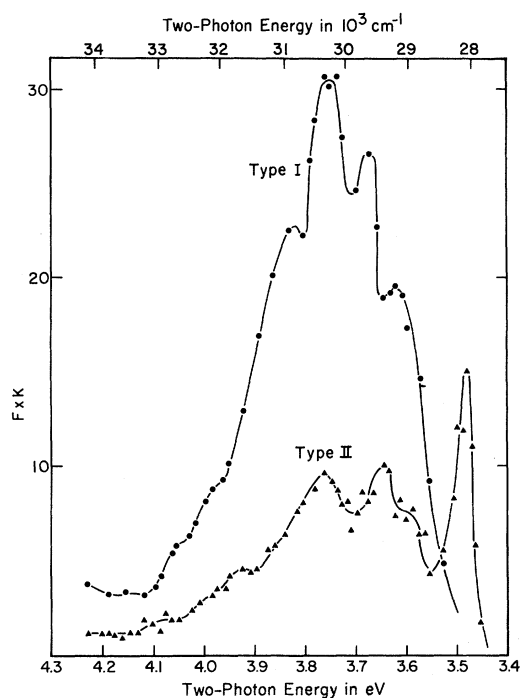


FIG. 3. The absorption constant  $K$  (calculated from the results of Fig. 2) is here multiplied by  $F = \alpha (E_{GI} - h\nu_v)^2 / h\nu_v$  using values of the electronic transition energies of the  $A_u$  and  $B_u$  levels of Ref. 19 for  $E_{GI}$  ( $E_{GI} = 3.1255$  eV for type-I spectra and  $E_{GI} = 3.1526$  eV for type-II spectra).

5 eV, however. On the other hand, the final states might be vibronic states. Their energy position arises then from a combination of odd-parity electronic states and odd-parity vibrations. The well-known electronic states at  $25\,300\text{ cm}^{-1}$  (3.13 eV) as well as a state of  $B_{3u}$  symmetry in the molecule,<sup>26</sup> calculated by Pariser,<sup>24</sup> are candidates.

We would like to thank Dr. Avakian and Dr. Sloan from the Dupont Research Laboratories for their most generous help in supplying single crystals of anthracene. We appreciate the efficient cooperation of Mr. James Hinton, Florida, as a commercial supplier of anthracene crystals.

\*Work supported by the Advanced Research Projects Agency and the U. S. Office of Naval Research.

†A preliminary report of this work was given at the 1966 International Quantum Electronics Conference at Phoenix, Arizona.

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<sup>1</sup>Warner L. Peticolas, John P. Goldsborough, and K. E. Rieckhoff, *Phys. Rev. Letters* **10**, 43 (1963).

<sup>2</sup>S. Singh and B. P. Stoicheff, *J. Chem. Phys.* **38**, 2032 (1963).

<sup>3</sup>S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, *J. Chem. Phys.* **42**, 330 (1965).

<sup>4</sup>John M. Worlock, in *Proceedings of the International Conference on the Physics of Quantum Electronics, Puerto Rico, 1965*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Company, Inc., New York, 1966).

<sup>5</sup>M. Iannuzzi and E. Polacco, *Phys. Rev. Letters* **13**, 371 (1964).

<sup>6</sup>M. Iannuzzi and E. Polacco, *Phys. Rev.* **138**, A806 (1965).

<sup>7</sup>W. L. Peticolas and K. E. Rieckhoff, *Phys. Letters* **15**, 230 (1965).

<sup>8</sup>Warner L. Peticolas, Robert Norris, and Klaus E. Rieckhoff, *J. Chem. Phys.* **42**, 4164 (1965).

<sup>9</sup>John P. Hernandez and Albert Gold, to be published. A. Gold and J. P. Hernandez, *Phys. Rev.* **139**, A2002 (1965).

<sup>10</sup>J. J. Hopfield, J. M. Worlock, and Kwangjai Park, *Phys. Rev. Letters* **11**, 414 (1963). J. J. Hopfield and J. M. Worlock, *Phys. Rev.* **137**, A1455 (1965).

<sup>11</sup>Dietmar Fröhlich and Herbert Mahr, *Phys. Rev. Letters* **14**, 494 (1965); *Phys. Rev.* **141**, 692 (1966).

<sup>12</sup>The type-I spectrum shown was obtained at about 10°K. All other type-I spectra were obtained at liquid nitrogen temperature. Only a very slight narrowing of the vibronic structure was observed upon cooling from liquid nitrogen temperature to about 10°K.

<sup>13</sup>The nomenclature used is defined in H. C. Wolf, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9.

<sup>14</sup>J. L. Hall, D. A. Jennings, and R. M. McClintock, *Phys. Rev. Letters* **11**, 364 (1963). Their value of  $K/N_L = 1.26 \times 10^{-29}$  cm sec/photon includes the quantum efficiency of the stimulated singlet fluorescence.

<sup>15</sup>Katsue Hasegawa and Susumu Yoshimura, *Phys. Rev. Letters* **14**, 689 (1965).

<sup>16</sup>S. Z. Weisz, A. B. Zahlan, J. Gilreath, R. C. Jarnagin, and M. Silver, *J. Chem. Phys.* **41**, 3491 (1964).

<sup>17</sup>M. Goepfert-Mayer, *Ann. Physik* **9**, 273 (1931).

<sup>18</sup>David A. Kleinman, *Phys. Rev.* **125**, 87 (1962).

<sup>19</sup>M. S. Brodin and S. V. Marisova, *Opt. i Spektroskopiya* **10**, 473 (1961) [translation: *Opt. Spectry. USSR* **10**, 242 (1961)].

<sup>20</sup>John W. Sidman, *Phys. Rev.* **102**, 96 (1956).

<sup>21</sup>Wolf, Ref. 13.

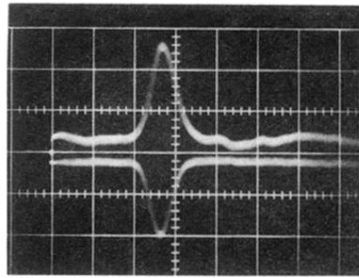
<sup>22</sup>D. P. Craig and P. C. Hobbins, *J. Chem. Soc.* **1955**, 539, 2302, 2309 (1955).

<sup>23</sup>The Davydov splitting of these two levels is even evident in the extrapolated values of Fig. 2.

<sup>24</sup>Rudolph Pariser, *J. Chem. Phys.* **24**, 250 (1956).

<sup>25</sup>The nomenclature used is the one given by Pariser in Ref. 24.

<sup>26</sup>This possibility was suggested to us by Professor A. C. Albrecht, Department of Chemistry, Cornell University.



<  $0.5 \mu \text{ sec}$  >

Time  $\longrightarrow$

FIG. 1. Coincidence of the laser signal (lower trace) and the two-photon absorption signal (upper trace). Absorption gives rise to an upward signal on the oscilloscope.