adsorption isotherm of Fig. 1 as follows: At the lowest coverages the positions of nitrogen molecules on the basal-plane surfaces of graphite are only weakly correlated. The change in slope slightly below A is associated with the formation of the registered, $\sqrt{3}$ phase. The second change in slope slightly above B coincides with completion of the $\sqrt{3}$ phase, i.e., with full registry. Beyond this point disordered inclusions appear as local regions are forced out of registry by the added gas molecules. The disordered regions increase at the expanse of those remaining ordered until, at a point slightly below D, a second layer begins to form. Long-range order then rapidly vanishes.

Although space does not permit us to present the data here, we found that when sufficiently cooled, the low-coverage phase, A, converted to a registered $\sqrt{3}$ structure. The high-coverage phase, E, on the other hand, formed a triangular array with a lattice constant smaller than that of the $\sqrt{3}$ phase. A detailed description of these and related measurements is now in preparation.

We are obligated to Dr. A. D. Novaco for directing our attention to the need for new methods of studying adsorbed phase structures and for sharing with us his knowledge of current theoretical and experimental developments in this field. We also wish to express our appreciation to Mr. T. Chung for assistance in preparing the sample.

---

*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. Bretz, J. G. Dash, D. C. Hickernell, E. O. McLean, and E. O. Vilches, Phys. Rev. A 8, 1529 (1973).

[2] *Monolayer and Submonolayer Helium Films*, edited by J. G. Daunt and E. Lerner (Plenum, New York, 1973).

[3] J. J. Lander and J. Morrison, Surface Sci. 6, 1 (1967).

[4] R. J. Rollefson, Phys. Rev. Lett. 29, 410 (1972).

[5] For a general review of experimental results see J. G. Dash, Progr. Surface Membrane Sci. 7, 95 (1973).

[6] Grafoil is the trademark of an expanded graphite product marketed by Union Carbide Products Division, 270 Park Avenue, New York, N. Y.

[7] H. H. Farrell, M. Strongin, and J. M. Dickey, Phys. Rev. B 6, 4703 (1972).

[8] S. Todireanu and S. Hautecler, Phys. Lett. 43A, 189 (1972).

[9] J. W. White, in *Proceedings of the Fifth IAEA Symposium on Neutron Inelastic Scattering, Grenoble, France, 1972,* (International Atomic Energy Agency, Vienna, 1972), p. 315.

[10] The wavelength employed for these measurements is considerably larger than the dimensions of the nitrogen molecule. Therefore the molecules act effectively as point scatterers.

[11] A. Thomy and X. Duval, J. Chim. Phys. 67, 286 (1970).

Direct Creation of Excitonic Molecules in CuCl by Giant Two-Photon Absorption*

G. M. Gale and A. Mysyrowicz†
Laboratoire d'Optique Quantique du Centre National de la Recherche Scientifique, 91405 Orsay, France

(Received 23 October 1973)

The two-photon absorption spectrum due to excitonic molecules is measured in CuCl at 77 and 4.2°K. We measured values of the two-photon transition cross section of the order of 10^{-44} cm^4 sec and estimated a peak value of 10^{-42}. The binding energy of the molecule is found to be 255 cm^{-1}.

The excitonic molecule, or biexciton, is an elementary excitation in semiconductors or insulators, consisting of two electrons and two holes. Recent calculations of its binding energy tend to show that it may exist for any electron-to-hole effective mass ratio.[1-3]

The previous experimental evidence for this particle was inferred indirectly from the observation of new emission lines, with quadratic-power-law dependence, in highly excited crystals.[4-8] Such lines are attributed to the radiative decomposition of biexcitons formed from the pool of high-density free carriers generated in the system. This type of evidence, however, permits other interpretations.[9] Also, one cannot deduce the molecular binding energy easily from the luminescence spectrum unless the luminescence decay mechanism is understood.

Here, we present another approach to the study of the excitonic molecule, namely by measuring its *absorption* spectrum. This is expected to yield an accurate value of the internal energy of the biexciton since it corresponds to a direct creation of this particle. In our experiment the excitation of the system occurs from the ground state to the molecular state via a two-photon absorption process. We also show that the corresponding transition cross section has an exceptionally large value, as predicted recently by Hanamura.[10]

Copper chloride was chosen for our investigation because this compound has a small electron-to-hole mass ratio[11] (0.02) which gives a large binding energy to the molecule, thus enabling it to be distinguished from the state consisting of two noninteracting free excitons.

Using the intense monochromatic radiation from a tunable dye laser, we measured directly the two-photon absorption cross section at several energies in the region $E = 2h\nu \simeq 2E_{\text{exc}} - B = E_M$. (Here E_{exc} represents the internal energy of a free exciton, E_M that of a biexciton, and B its binding energy.) This can be readily achieved by measuring the intensity of a parallel propagating beam transmitted through the sample in function of the incident intensity.

The total loss in the medium may be expressed as

$$dF(z)/F(z) = -N\,dz\,[\sigma + \delta F(z)], \tag{1}$$

where $F(z)$ is the photon flux, σ and δ are the one- and two-photon cross sections, respectively, and N is the number of unit cells per unit volume. The loss equation has a solution of the form

$$F_0/F = e^{\sigma N l}[1 + (\delta F_0/\sigma)(1 - e^{-\sigma N l})], \tag{2}$$

where F_0 is the incident and F the transmitted flux.

A plot of F_0/F versus F_0 yields a straight line. σ is obtained from the intercept at $F_0 = 0$ and δ from the slope of the line.

The dye laser used is schematically depicted in Fig. 1. The active medium is a $10^{-3}M$ solution of 3, 3′-dimethyl-2, 2′ oxatricarbocyanine iodide in acetone, contained in a 1-cm-thick cell at Brewster's angle, and pumped off-axis[12] by a giant ruby laser pulse. Tuning of the frequency is achieved with a grating in the cavity. The second harmonic of the output beam is generated in an ammonium dihydrogen phosphate (ADP) crystal oriented for phase-matching conditions, and provides the intense emission in the required spectral region. Typical characteristics for the blue radiation are as follows: intensity 200 kW, pulse duration 16×10^{-9} sec, spectral width ~6 cm^{-1}, tunable between 25 440 and 26 040 cm^{-1}. The measurements were carried out on two different single crystals, at 77 and 4.2°K. In every case, the plot of F_0/F versus F_0 gave rise to straight lines, as expected from Eq. (2). The resulting values of σ and δ are shown in Table I. The sudden increase of δ in a region well below the first excitonic absorption line (at 25 865 cm^{-1} for 4.2°K and 26 008 cm^{-1} for 77°K) indicates a strong two-photon resonance. We could not measure δ at higher energies, because of the rapid increase of σ, even with a 0.37-mm thin sample.

However, whenever *nonlinear* absorption was appreciable, we noticed the appearance of a strong luminescence in the sample, similar to that observed under very high excitation in the absorption continuum. It consisted of one band at 25 610 cm^{-1} at 77°K and of four lines, at A

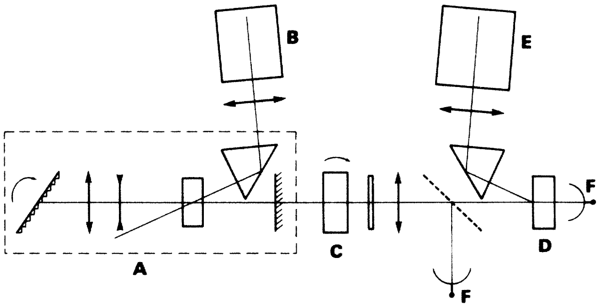

FIG. 1. Experimental setup: A, dye laser; B, ruby laser; C, ADP crystal; D, sample at 4.2 or 77°K; E, monochromator; F, photocell.

TABLE I. One- and two-photon absorption cross sections of CuCl as a function of frequency at 77 and 4.2°K. Also shown is the separation of the incident photon frequency from that of the $n = 1$ exciton absorption line.

ν 77°K	$\Delta\nu$ (cm^{-1})	$\sigma\times10^{22}$ (cm^2)	δ (cm^4 sec)
25,525	483	0·0	$<3\times10^{-49}$
25,592	416	0·33	6×10^{-48}
25,668	340	0·40	5×10^{-47}
25,711	297	1·7	9×10^{-47}
25,745	263	38·5	$1{\cdot}2\times10^{-45}$
25,788	220	75·0	5×10^{-45}
25,796	212	84·6	7×10^{-45}
ν 4·2°K	$\Delta\nu$ (cm^{-1})	$\sigma\times10^{22}$ (cm^2)	δ (cm^4 sec)
25,491	374	1·1	8×10^{-48}
25,609	256	17·3	8×10^{-45}
25,651	214	63·5	3×10^{-44}

$=25\,647$, $B=25\,567$, $C=25\,522$, and $D=25\,370$ cm^{-1}, at 4.2°K. Although a complete interpretation of this emission spectrum has not yet been given, the main line C has been previously attributed to the decomposition of molecules into photons and $n=1$ excitons.[5]

We recorded, in a second experiment, this luminescence intensity as a function of input photon energy, up to $h\nu = E_{\text{exc}}$ for a fixed incident intensity of 100 kW from the same dye laser. The emission from the front surface could easily be detected either photographically or photometrically through an $f/10$ monochromator. Results at 4.2 and 77°K, corrected for reflection losses, are shown in Fig. 2.[13] As one can see, the emission intensity reaches a maximum for both temperatures at a frequency separation $\Delta\nu = 127$ cm^{-1} from the $n=1$ exciton absorption peak, declining rapidly at smaller energy separations. We measured a luminescence quantum efficiency at the peak of the excitation curves 30 times larger than for an excitation of the same intensity falling in a strong absorption region at 28 810 cm^{-1}.

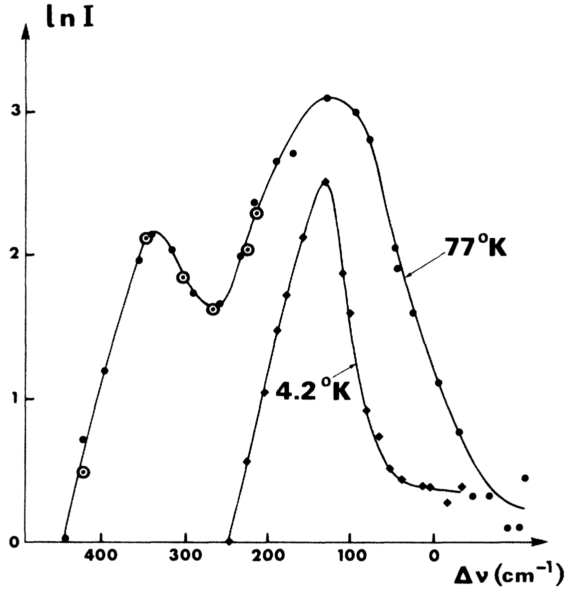

FIG. 2. The two-photon excitation spectrum of CuCl at 77 and 4.2°K. The natural logarithm of the molecular emission intensity is plotted versus the difference between the $n=1$ exciton absorption-line frequency (26 008 at 77°K, 25 865 cm^{-1} at 4.2°K) and that of the incident light. The open circles are obtained from the direct measurement of δ.

We now compare the direct measurement of δ with the two-photon excitation curve obtained in the same spectral region. To do so, we compute the quantity

$$I_M = C\int_0^l \tfrac{1}{2}\delta k N F^2(z)\,dz, \tag{3}$$

which represents the emission intensity due to the total number of molecules created up to depth l in the crystal by two-photon absorption, and collected by the detection channel. Here k is the quantum efficiency and C a collecting factor. In our case, l corresponds to the sample thickness.

Substituting $F(z)$ from Eq. (2) and integrating yields

$$I_M = Ck\frac{F_0}{2}\left[\frac{(1+\epsilon)(1-e^{-\sigma N l})}{1+\epsilon(1-e^{-\sigma l})} - \frac{\ln[1+\epsilon(1-e^{-\sigma N l})]}{\epsilon}\right], \quad \epsilon = \frac{\delta F_0}{\sigma}. \tag{4}$$

In Fig. 2 we have plotted (open circles) the results of the calculated emission intensity from Eq. (4) using the experimentally measured values of δ given in Table I and fitting the factor C at a single point. A constant quantum efficiency has been assumed. The excellent agreement between the dispersion of δ and the two-photon excitation curve allows us to deduce the internal energy of the molecule from the peak position of Fig. 2.[14] We find $E_M = 2h\nu_0 = 51\,764$ cm^{-1} at 77°K and 51 475 cm^{-1} at 4.2°K and a binding energy $B = E_M - E_{\text{exc}} = 255$ cm^{-1}, a value significantly different from that obtained from the luminescence spectrum.[15] A calculation of B, using the formulas of Refs. 1 and 2, gives values ranging between 150 and 370 cm^{-1}, depending on the choice of the dielectric constant (static or optic) for the exciton and the molecule.[16]

We also estimate the peak δ value to be $\delta \sim 10^{-42}$ at 4.2°K. This is an exceptionally large cross section leading to a nonlinear absorption coefficient of the order of 10^5 cm^{-1} with a light flux of 10^{25} photons/cm^2. This value is in good agreement with a recent calculation of Hanamura.[10] As pointed out by this author, there are two reasons for such giant two-photon transition probabilities. The first is simply the proximity of the $n=1$ excitonic level, acting as a quasiresonant intermediate state, and contributing by a factor 10^3 to the enhancement. The second enhancement occurs because of the particular type of transition, in which two electrons (within approximately a molecular radius of each other) are simultaneously promoted to the conduction band.

Finally, we tentatively interpret the secondary peak, observed at 77°K in the region $\Delta\nu = 377$ cm^{-1}, as a two-phonon-assisted, two-photon transition to the molecular state. This peak is separated from the main peak by the frequency of one longitudinal optical phonon ($\Omega = 210$ cm^{-1}) in the one-photon frequency scale of Fig. 2 and disappears, as expected, at 4.2°K, where the thermal population of phonons is negligibly small. We believe that this transition is favored over the one involving only one phonon, not apparent here, because of the k-dependent matrix element between exciton and molecule.[17] A somewhat similar situation is encountered in the radiative decay of free excitons involving one and two phonons.

In conclusion, we have brought new experimental evidence for the existence of the excitonic molecule in CuCl by studying its absorption spectrum. We have shown that this particle is responsible for an unusually large nonlinear response of the medium.

We acknowledge fruitful discussions with Professor J. Ducuing, Dr. C. Flytzanis, and Professor Y. R. Shen. We are very grateful to Professor D. Fröhlich for providing us with good quality samples and to Dr. K. Cho for communication of a preprint of his work.

---

*Preliminary results have been reported at the Colloque sur les Semiconducteurs à Grand Gap, Montpellier, France, 5–8 September 1973.

†Now on leave at the Department of Physics, University of California, Berkeley, Calif. 94720.

[1] R. K. Wehner, Solid State Commun. 7, 457 (1969).

[2] O. Akimoto and E. Hanamura, Solid State Commun. 10, 253 (1972).

[3] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. B 8, 1570 (1973).

[4] J. R. Haynes, Phys. Rev. Lett. 17, 860 (1966).

[5] A. Mysyrowicz, J. B. Grun, R. Levy, A. Bivas, and S. Nikitine, Phys. Lett. 26A, 615 (1968); R. S. Knox, S. Nikitine, and A. Mysyrowicz, Opt. Commun. 1, 19 (1969).

[6] H. Souma, T. Goto, and M. Ueta, J. Phys. Soc. Jap. 31, 1285 (1971); C. I. Yu, T. Goto, and M. Ueta, J. Phys. Soc. Jap. 32, 1671 (1972).

[7] S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid State Commun. 12, 223 (1973).

[8] J. F. Figueira and H. Mahr, Phys. Rev. B 7, 4520 (1973).

[9] See Ref. 4 and the *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, Poland, 1972,* edited by the Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw, 1972).

[10] E. Hanamura, Solid State Commun. 12, 951 (1973).

[11] K. Song, Suppl. J. Phys. (Paris) 28, C3-43 (1967); J. Ringeisen and S. Nikitine, *ibid.*, C3-48 (1967).

[12] D. J. Bradley, A. J. F. Durrant, G. M. Gale, M. Moore, and P. D. Smith, IEEE J. Quantum Electron. 4, 707 (1968).

[13] At 4.2°K, we have plotted the intensity of line D, because it is conveniently located at a lower frequency. The other lines show a similar behavior, namely a peak in the excitation curve for $\Delta\nu = 127$ cm^{-1}. At 77°K, the integrated intensity of the emission band is plotted.

[14] We have verified that the peak position of the excitation curve is insensitive to the value of σ. However, the linear losses flatten the excitation curve, increasing its half-width.

[15] A detailed discussion of the molecular luminescence in CuCl will be published elsewhere.

[16] The $n = 1$ exciton radius is ~7 Å in CuCl and therefore a value of the dielectric constant close to the optic constant must be used [H. Haken, Fortschr. Phys. 38, 271 (1958).] For the molecule, which has larger dimensions, one expects an intermediate value. This complication in the calculation of the binding energy of the molecule does not appear to have been considered in Refs. 1–3.

[17] K. Cho, Opt. Commun. 8, 412 (1973).