Two-Photon Molecular Spectroscopy

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The spectroscopist's job is to find and to describe the excited states of molecules. Many excited states interact strongly with light and are easy to find, whether or not they are easy to describe. Such states are the usual meat of spectroscopy. But there are other excited states, interacting only weakly with light, which are very important to an understanding of many physical and chemical processes. Perhaps the most well-known examples are the molecular triplet states, which rarely contribute to the visible color of a substance, but which may dominate the photochemistry. There are also other types of "forbidden" states which exert their invisible influence over photochemistry and other radiationless processes, and it is also the spectroscopist's job to find them and to describe them.

Here we give an Account of the foundations of a new branch of spectroscopy which is devoted to finding and describing electronic excited states which are "geometrically forbidden" to the rest of spectroscopy. Strictly speaking, these states occur only in atoms and in molecules and crystals possessing a center of symmetry, but similar weakly colored staes can exist in any molecule. They are the electronic g states (g for gerade). They are those states for which the electronic wave function remains unchanged when the Cartesian coordinate system of the molecule in inverted through the center of symmetry.

An example of some one-electron wave functions on the naphthalene framework is given in Figure 1. The g states are easy to pick out, because they are the ones that have identical lobes across the center of symmetry for each other.

Half the electronic states in Figure 1 have g character. The other half have u character (u for ungerade). The u wave functions have lobes of the same shape but of opposite sign across the center of symmetry from each other; the function changes sign as a whole upon coordinate inversion.

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The exact many-electron wave functions of naphthalene cannot be diagrammed on these pages, for they need a space of much higher dimensionality. However, they, too, are rigorously divided into two classes of states distinguished by g and u character. The g states are unchanged under inversion operations in the many-dimensional space; the u states are changed in sign. The two classes are about equally numerous.

How does the inversion symmetry of a state exert its influence over that state's interaction with light? Quantum theory says that this question must be posed for pairs of states, and that the interaction strength parameter linking states o and f is

$$M_{of} = \int \psi_o{}^*(r)\mathbf{r}\psi_f(r)d\tau_r, \tag{1}$$

We will always take the original state o to be the molecule's ground state, which is nearly always a g state. In Figure 2 we perform some integrals like eq 1 for some naphthalene-like states of Figure 1.

The diagrams show that when we consider a g to u transition, some component(s) of M_{of} will not vanish, but when we try a g to g transition, every component of M_{of} vanishes. This is a very general property, true for the exact many-electron wave functions as well as for our diagrammatic one-electron examples. It results in the famous parity rule of one-photon spectroscopy: *transitions from g to u or from u to g are allowed; transitions from g to g or from u to u are forbidden.*

None of the excited g states of naphthalene can be unequivocally observed by one-photon spectroscopy, either in absorption or emission, because of this rule. This certainly represents a loss to theory, for the experimental location of these states would give new fundamental checks on the validity of various calculational and theoretical methods.

As we shall now see, this "other half" of spectroscopy is exactly what can be investigated by simultaneous two-photon absorptions.

The Two-Photon Phenomenon

In 1931 Maria Göpper-Mayer first realized that an atom or a molecule could absorb two photons simultaneously in the same quantum act.[1] She was working with Dirac's new treatment of absorption, emis-
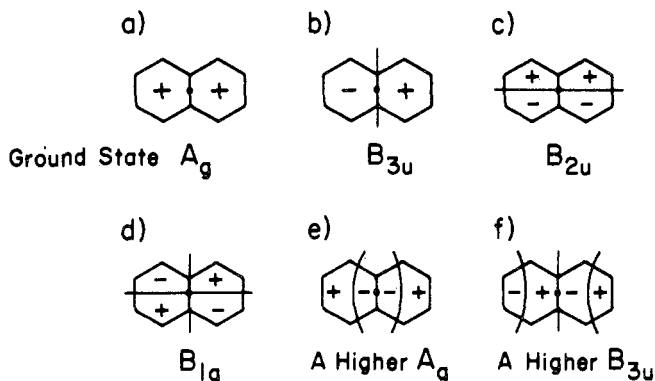
Figure 1. Some possible nodal patterns for one-electron states on a naphthalene framework.

Figure 2. Diagramatic calculation of the transition moment of two naphthalene-like one-electron transitions, one allowed and one forbidden.

sion, transmission, and scattering of light according to the quantum mechanical picture. Dirac had already realized that first-order perturbation theory of the effect of light on matter yielded terms describing the absorption and emission of single photons. Further, second-order perturbation theory gave terms which Dirac recognized as representing transmission and scattering. The quantum picture was that scattering was a *two-photon process* of simultaneous destruction and creation of a pair of photons. The frequencies could be the same (Rayleigh) or different (Raman). Indeed, both frequency and direction of the two photons could be the same, in which case the picture described the transmission of light with altered velocity and gave a formula for the index of refraction. Because of this, the treatment became known as "Dirac dispersion theory."

However, it was left to Göppert-Mayer to realize that Dirac dispersion theory also described some other two-photon processes that had never been imagined before—the simultaneous emission of two photons, or the simultaneous absorption of two photons.

The quantum picture of two-photon absorption is roughly as follows. Suppose each of two photons λ and μ by itself produces only very small nonresonant electrical oscillations in a molecule as it passes by, at frequency ω_λ or ω_μ. If λ and μ are both present simultaneously, the oscillations can be thought of as due to the sum and difference frequencies. If $\omega_\lambda + \omega_\mu$ is a resonant frequency of the molecule, the small oscillations at that frequency can get out of hand and set up an electromagnetic field that cancels that of the two photons. Thus the two photons are destroyed simultaneously and the molecule is raised to an excited state.

This picture is very similar to the picture for a one-photon excitation. There is a crucial difference, however, in the geometry of the process. A single photon can raise only oscillations of u symmetry in a centrosymmetric molecule, because the interaction parameter is $\mathbf{M}_{of}$. One can visualize these oscillations by thinking of water sloshing in a naphthalene-shaped pond, with nodal patterns given by the B_{3u} or B_{2u} diagrams of Figure 1b,c. However, if two such photons work together perpendicularly, they can raise an oscillation of symmetry B_{1g}, as in Figure 1d. If two photons work together in parallel to raise two

B_{3u}'s (Figure 1b,f), then the result will have symmetry A_g, as in Figure 1e.

When Göppert-Mayer stated all of this in Dirac's language,[1] she found that the two-photon absorption coefficient was the square of an expression having numerators like $M_{oi}{}^x M_{if}{}^z$, where the M's are components of the vectors from the one-photon theory. Here again o is the original (ground) state, f is the final state, and i is an "intermediate state," and must be summed over. This numerator provides the two-photon selection rule, as follows: If o is a g state, then i must be a u, or M_{oi} will vanish. But if i is a u state, then f must be a g state, or the second factor M_{if} will vanish. *Thus for two-photon transitions, g to g is allowed, but g to u is forbidden.* This is the exact opposite of the one-photon selection rule.

This selection rule opens the possibility of a new spectroscopy, which will do for molecular g states what the old spectroscopy does for molecular u states. It is intrinsically as rich in molecular information as one-photon spectroscopy is, and will possess all the same subfields: vibronic, excitonic, etc.

Lest this be thought an exaggeration, let us recall that two-photon absorption theory is almost identical with Raman scattering theory. It is well known that Raman spectroscopy is specific for molecular vibrations of g symmetry, while infrared absorption is specific for the u vibrations. We are simply saying that two such complementary spectroscopies are also possible in the electronic manifold, and noting that all the usual complications of electronic spectroscopy will be present in the new field.

The Two-Photon Tensor

In one photon spectroscopy the molecular property of interest is the transition moment $\mathbf{M}_{of}$, a vector in three dimensions. To get the extinction coefficient ϵ for photons of polarization λ, one forms the quantity

(1) M. Göppert-Mayer, *Ann. Phys.*, 9, 273 (1931).

$$\epsilon \propto |\boldsymbol{\lambda} \cdot \mathbf{M}_{of}|^2 \qquad (2)$$

Table I
Tensor Patterns for the Four Allowed Two-Photon Transitions from an A_g Ground State for a Molecule or Crystal of Symmetry Group D_{2h} (Naphthalene)[a]

$$A_g \leftarrow A_g \qquad S = \begin{pmatrix} s_1 & 0 & 0 \\ 0 & s_2 & 0 \\ 0 & 0 & s_3 \end{pmatrix}$$

$$B_{1g} \leftarrow A_g \qquad S = \begin{pmatrix} 0 & s_4 & 0 \\ s_5 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$B_{2g} \leftarrow Ag \qquad S = \begin{pmatrix} 0 & 0 & s_6 \\ 0 & 0 & 0 \\ s_7 & 0 & 0 \end{pmatrix}$$

$$B_{3g} \leftarrow Ag \qquad S = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & s_8 \\ 0 & s_9 & 0 \end{pmatrix}$$

[a] In naphthalene two of the B_g's would involve out-of-plane excitations and would lie at very high energies.

In two-photon spectroscopy the molecular property is a transition tensor S_{of}. It is a three by three matrix whose elements are basically the products $M_{oi}^x M_{if}^x$, $M_{oi}^x M_{if}^y$, ..., $M_{oi}^z M_{if}^z$. To get the extinction coefficient δ for photons of polarization λ and μ, one forms the quantity

$$\delta \propto |\lambda \cdot S_{of} \cdot \mu|^2 \qquad (3)$$

It turns out that the symmetry of the transition plays a large role in determining what the tensor S looks like. For instance, in a crystal of D_{2h} symmetry, it is possible to have transitions to states of symmetry A_g, B_{1g}, B_{2g}, or B_{3g}. A_g has the full symmetry of a rectangular parallelopiped, while the B_g's all have a pair of perpendicular nodal planes. The tensors corresponding to these four symmetry types are given in Table I. The zero elements, which set the tensor "pattern," are determined completely by symmetry.

These different patterns give rise to some amusing polarization effects. In Table II we show how polarization may be used in a crystal of D_{2h} symmetry to determine whether an observed transition is of type $A_g \leftarrow A_g$ or of type $B_g \leftarrow A_g$. There is no absorption at all, even when the transition is allowed, if the photons are polarized so that they act in an ineffective geometry. The results of Table II are obtained by using the tensor patterns of Table I in eq 3 along with the appropriate unit vectors representing polarization.

These tests (and their elaborations) are empirical diagnostics for the symmetry species of two-photon excitations of a D_{2h} crystal. An extensive tabulation of results like those in Table II has been given by Inoue and Toyozawa[2b] and by Bader and Gold.[2c] They treat all 32 crystal point groups. Several experimental papers have appeared which make use of this technique, most notably from the laboratory of Dietmar Fröhlich at Dortmund.[3]

Randomly Oriented Samples

In molecular spectroscopy one can often obtain important experimental and theoretical simplifica-

(2) (a) L. N. Ovander, *Opt. Spectry.*, 9, 302 (1960); (b) M. Inoue and Y. Toyozawa, *J. Phys. Soc. Jap.*, 20, 363 (1965); (c) T. R. Bader and A. Gold, *Phys. Rev.*, 171, 997 (1968); (d) W. M. McClain, *J. Chem. Phys.*, 55, 2789 (1971).

(3) (a) D. Fröhlich, B. Staginnus, and S. Thurm, *Phys. Stat. Solidi*, 40, 287 (1970); (b) D. Fröhlich, B. Stagginus, and E. Schönherr, *Phys. Rev. Lett.*, 19, 1032 (1967).

Table II
Polarization Dependence of Two-Photon Absorption for Photons Traveling down the z Axis of a Crystal (Rectangular Parallelopiped)

Transition symmetry	Polarization	
	Both photons x polarized	One x polarized, one y polarized
$A_g \leftarrow A_g$	$s_1{}^2$	0
$B_g \leftarrow A_g$	0	$s_5{}^2$

tions by working with a gaseous or liquid sample rather than with a crystalline material. This is doubly true in two-photon spectroscopy, where path lengths of several centimeters or more may be needed to see the effect and where the intense light may destroy a carefully nurtured crystal in a single catastrophic shot. Hence we will now consider the effect of orientation averaging on the observed cross section.[4]

Looking at eq 2 and 3 for ϵ and δ, one can see that these quantities take variable values depending on the orientation of the molecule relative to λ, or to λ and μ. When an orientation average is performed on ϵ, the answer is

$$\langle \epsilon \rangle = {}^1/_3 (\lambda \cdot \lambda^*)(M \cdot M^*) \qquad (4)$$

where, of course, $\lambda \cdot \lambda^* \equiv 1$ for all polarization. This is the explanation of the familiar fact that ordinary dye colors are independent of the polarization of the light by which they are viewed.

However, it has long been recognized that there is a residual polarization effect for all kinds of two-photon optical events, such as scattering and fluorescence. It is the basis of the polarization ratio technique of Raman scattering, or of the photoselection technique of luminescence and solid-state photochemistry. Thus when the orientation average is performed on eq 3 the polarization dependence does *not* vanish. It is given by

$$\langle \delta \rangle = \delta_F(-|\lambda \cdot \mu^*|^2 + 4|\lambda \cdot \mu|^2 - 1) + \delta_G(-|\lambda \cdot \mu^*|^2 - |\lambda \cdot \mu|^2 + 4) + \delta_H(4|\lambda \cdot \mu^*|^2 - |\lambda \cdot \mu|^2 - 1) \qquad (5)$$

The first thing to notice is that *three* molecular parameters survived the averaging, where there was but one in eq 4. We call them

$$\delta_F = S_{\alpha\alpha} S_{\beta\beta}{}^* = \left| \sum_1^3 \text{diagonal elements} \right|^2 \qquad (6a)$$

$$\delta_G = S_{\alpha\beta} S_{\alpha\beta}{}^* = \sum_1^9 |\text{each element}|^2 \qquad (6b)$$

$$\delta_H = S_{\alpha\beta} S_{\beta\alpha}{}^* = \sum_1^9 (\text{hermitian products}) \qquad (6c)$$

where the subscripts α and β stand for x, y, z and repeated indices are summed.

The second thing to notice in eq 5 is that $\langle \delta \rangle$ is a linear function of *two* variables, $|\lambda \cdot \mu^*|^2$ and $|\lambda \cdot \mu|^2$. We shall first discuss how to use these variables to measure δ_F, δ_G, and δ_H; then we will discuss what the measured values say about the transition symmetry.

The variables $|\lambda \cdot \mu^*|^2$ and $|\lambda \cdot \mu|^2$ are identical only when λ and μ are real—that is, when they represent linearly polarized photons. Circular photons are rep-

(4) (a) P. R. Monson, and W. M. McClain, *J. Chem. Phys.*, 53, 29 (1970); (b) P. R. Monson and W. M. McClain, *ibid.*, 56, 4817 (1972).

Table III
Assignment Rules for Two-Photon Processes in Liquids or Gases[a]

Case	Indicators			Molecular symmetry groups					
	δ_F	$\delta_G - \delta_H$	$\delta_G + \delta_H$	C_2	D_{2h}	C_4	D_4	$D_{\infty h}$	O_h
1	+	+	+	A		A			
2	+	0	+		A_g		A_1	$\Sigma_g{}^+$	A_{1g}
3	0	+	+	B	(B_{1g}, B_{2g}, B_{3g})	E	E	π_g	
4	0	0	+			B	(B_1, B_2)	Δ_g	(E_g, T_{2g})
5	0	+	0				A_2	$\Sigma_g{}^-$	T_{1g}

[a] The indicators must be measured and the group of the absorbing entity must be known; then assignments for allowed transitions can be made with only occasional ambiguities.
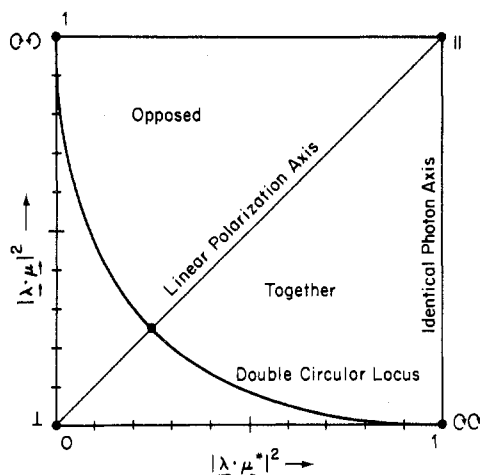

Figure 3. The experiment plane. Every point corresponds to one or more polarization experiments; every experiment, to a point.

resented by complex polarization vectors like $2^{-1/2}$ $(1, \pm i, 0)$, which represent right or left light propagating in the z direction. This comes from the basic formula for the electric field of an electromagnetic wave

$$\mathbf{E}(\mathbf{r},t) = E_0 \mathrm{Re}\{\boldsymbol{\lambda} \exp i(\mathbf{k}\cdot\mathbf{r} - \omega t + \phi)\} \qquad (7)$$

as can be seen by substitution.

It seems natural to define a space with the variables $|\boldsymbol{\lambda}\cdot\boldsymbol{\mu}^*|^2 = x$ and $|\boldsymbol{\lambda}\cdot\boldsymbol{\mu}|^2 = y$ as axes. Since both $\boldsymbol{\lambda}$ and $\boldsymbol{\mu}$ are complex *unit* vectors, $(\boldsymbol{\lambda}\cdot\boldsymbol{\lambda}^* \equiv 1)$, the Schwartz inequality tells us immediately that x and y can take only values between 0 and 1; in other words, that all possible experiments lie in a unit square of the x,y space. We show a map of this space as Figure 3, and we call it the *experiment plane* of two-photon spectroscopy. The four corners of the plane have a particular meaning. Corner $(0,0)$ represents the absorption of two photons polarized perpendicular to each other; corner $(1,1)$ is the case of two parallel linear photons. Corner $(0,1)$ represents contrarotating circular photons (propagating parallel), while $(1,0)$ is for corotating circular photons, propagating parallel.

Three noncollinear points determine a plane in three dimensions, so any three polarization experiments *whose points are not collinear on the experiment plane* may be used in principle to measure the three fundamental spectra. Once this has been done, there is nothing left to learn from further polarization experiments, so we say that three such experiments are a *complete polarization study*.

In practice, the more broadly based the three points are, the better—and one cannot do better than to use three of the corner points.

An important criterion for the design of *complete* two-photon experiments may be derived from the noncollinear requirement. All the experiments representing the absorption of two identical photons lie along the right-hand edge of the square, and cannot form the basis of a complete study. This is consonant with the fact that the tensor must be symmetric in this case, so in a sense variability along one line is all that is needed. However, transitions which have no geometrical reason for the tensor symmetry cannot be distinguished from those that do, so the identical photon absorption experiment is an inherently more limited tool than independent photon absorption. This is a pity, for this is by far the easiest kind of experiment to do, using a tunable dye laser source and detecting the absorption by fluorescence.

Determination of Transition Symmetries in Randomly Oriented Samples

Let us now return to the basic question which motivated the preceding development: is it possible to tell an $A_g \leftarrow A_g$ from $B_g \leftarrow A_g$ transition when the molecules are randomly oriented? We saw that this was easy for crystalline absorbers, but is such information preserved in liquids?

The answer is *yes;* the distinction between different transition symmetries is well preserved in liquids. Looking back at Table I, we see that only the $A_g \leftarrow A_g$ transition has a nonzero trace, which means that only these transitions will have their δ_F different from zero; hence we can tell the totally symmetric A_g transitions from the nontotally symmetric B_g ones.

This technique may be generalized to molecules of more complicated symmetry than D_{2h}. An abbreviated table of the results is given as Table III, in which it may be seen that nearly every transition symmetry may be distinguished empirically by complete polarization studies. A more detailed table, with the method of derivation, is given in ref 2d.

Two-Photon Spectroscopy in Practice

Two types of two-photon experiments should be strongly distinguished from the outset: the direct absorption experiment[5] and the fluorescence detected experiment.[6] These methods, as practiced in the author's laboratory, are shown diagrammatically in Figures 4 and 5 and are explained in the captions. Direct absorption is more difficult but more reward-

(5) (a) J. J. Hopfield, J. M. Worlock, and K. Park, *Phys. Rev. Lett.*, 11, 414 (1963); (b) B. Staginnus, D. Frölich, and T. Caps, *Rev. Sci. Inst.*, 39, 1129 (1968).

(6) (a) W. Kaiser and C. G. B. Garrett, *Phys. Rev. Lett.*, 7, 229 (1961); (b) I. Webman and J. Jortner, *J. Chem. Phys.*, 50, 2706 (1969); (c) R. P. Drucker and W. M. McClain, in preparation.
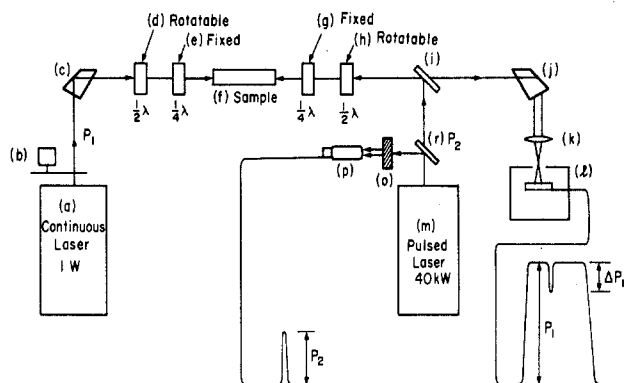
Figure 4. An apparatus for complete polarization studies by the absolute method. Probe beam power P_1 is from a continuous gas laser (a) operated so that its intensity fluctuations are below the limit of detectability. This "probe" beam is chopped (b) to avoid destruction of the detecting diode, passes through a dispersing prism (c), a pair of phase retardation prisms (Fresnel rhombs) (d and e) which control the polarization, then into the sample (f), and finally into a fixed-frequency, diffraction-limited monochromator (j, k, and l). The power beam P_2 originates in pulsed laser (m), which is a tunable dye laser pumped by a single mode oscillator-amplifier ruby system, with frequency doubling. The power is monitored by n, o, p; the beam is made coaxial with the probe beam by the special coated beam splitter (i), the polarization is controlled by retardation prisms (h and g); it then passes through the sample (f) and is finally thrown out to a beam stop by dispersing prism (c). The three data from each shot P_1, ΔP_1, and P_2 are read digitally by an automatic peak height measuring system.

ing in that it yields absolute values of the δ's and can be used to carry out complete polarization studies. On the other hand, fluorescence detection has the advantage that far fewer absorption events can be detected, but it yields only relative values of the δ's, unless assumptions are made about the quantum yield of the two-photon excited fluorescence process. Also, in practical terms, one is presently limited to the absorption of two identical photons by this method, with consequent limitations explained in the preceding section.

In the future it may be possible to perform complete polarization studies by the fluorescence method. It will be necessary to use a strong beam with $h\nu_1 < \frac{1}{2}\Delta E$ and a weak beam with $h\nu_2 > \frac{1}{2}\Delta E$. The sample will be in rigid or viscous solution. The polarization theory of this experiment is already worked out.[7]

The two-photon absorption strength δ is defined experimentally by the relation

$$-\Delta P_1 = -\Delta P_2 = P_1 P_2 \delta C l A^{-1} \qquad (8)$$

in the two-beam case, where P_1 and P_2 are optical powers, ΔP_1 and ΔP_2 are absorbed powers, all expressed in photons per second. C is sample concentration, l is path length, and A is beam area. The usual units of δ are cm^4 sec photon^{-1} molecule^{-1}, and a typical size is about 10^{-50} in these units. In our laboratory we usually say 10^{-50} cm^4 sec photon^{-1} molecule^{-1} is 1 maria, in honor of Maria Göppert-Mayer.

The small size of the maria presents experimental two-photon spectroscopy with its primary challenge. Let us examine some order-of-magnitude calculations to see why.

In the two-beam case, realistic values would be $\Delta P_1/P_1 = 10^{-2}$ (a 1% dip in the probe beam), $\delta = 1$

(7) (a) W. M. McClain, J. Chem. Phys., 57, 2264 (1972); (b) W. M. McClain, ibid., 58, 324 (1973).
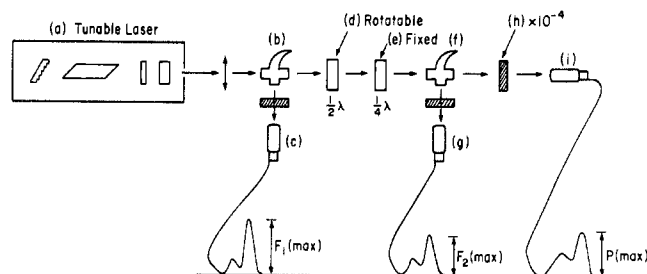

Figure 5. An apparatus for polarization studies of two-photon excited fluorescence. The light is a tunable pulsed laser (a) which produces vertically polarized light. This passes into the first sample (b) and the fluorescence F_1 is detected at c. The polarization is then altered by retardation prisms (d and e) so that in the second sample (f) the light may be vertical or horizontal, or right or left circular. The second sample fluorescence, F_2, is monitored at g, and the beam power P is monitored at i. The primary data are the peak heights F_1(max) and F_2(max); their ratio gives information on the symmetry of the absorbing transition. The ratio F_1/F_2 is not greatly affected by poor beam quality. The ratios F_1/P^2 or F_2/P^2 are affected by beam quality, however.

$\Gamma_1^+: -\blacktriangle-\blacktriangle-; \ \Gamma_3^+: -\bullet-\bullet-; \ \Gamma_4^+: -\circ-\ \circ-;$
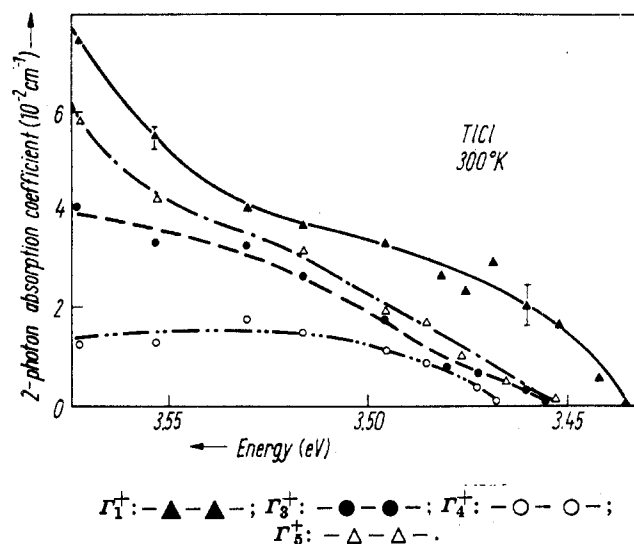$\Gamma_5^+: -\triangle-\triangle-.$

Figure 6. Two-photon spectrum of crystalline TlCl at 300 K, symmetry group O_h. The spectrum is decomposed by polarization methods into contributions by the different allowed symmetry species. The two-photon absorption starts at 3.43 eV as a pure A_{1g} or Γ_1^+ excitation. The one-photon spectrum starts at a slightly lower energy and is therefore of type s → s, while the two-photon exciton seen here must be of type s → p. The authors conclude that the valence and conduction bands in TlCl are of opposite parity. This could not have been deduced in an O_h crystal without the two-photon result, because the crystal itself is optically isotropic and there is no one-photon way to tell whether a given exciton band is of s or p type. The spectrum is photographically reproduced from ref 3a (with permission of Phys. Rev. Lett.). The ordinate is probe beam extinction constant at a laser flux of 10^{26} photon/cm^2 sec; 1×10^{-2} cm^{-1} = 0.570 maria for TlCl crystal.

maria = 10^{-50} cm^4 sec, $C = 10^{22}$ molecule cm^{-3} (a neat sample liquid), $l = 10$ cm, and $A = 10^{-2}$ cm^2. Equation 8 then requires that P_2 be 10^{23} photons sec^{-1}, or about 40 kW at 5000 Å in the green. This is an intensity of 4 MW cm^{-2}. Clearly this is achievable only with a pulsed laser, but it is low enough that one can avoid destruction of a well-cleaned sample liquid, and it is low enough to avoid self-focusing, filamentation, and stimulated scattering in most liquids. Experiments have been performed successfully at powers ten times greater, samples can be ten times longer, and probe beam dips of a hundredth of a per cent can be detected.[8] Putting all

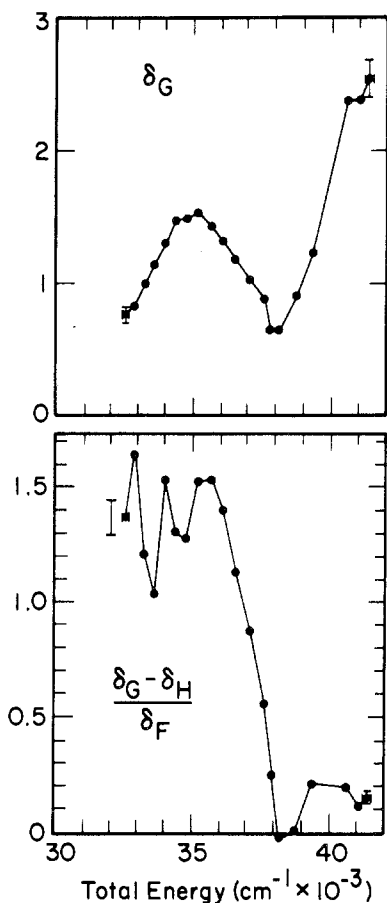(8) R. L. Swofford and W. M. McClain, Rev. Sci. Inst., 44, 978 (1973).

Figure 7. Two-photon spectrum of neat liquid 1-chloronaphthalene at 300 K, measured by the direct method.[4b] The best measure of total intensity is δ_G, which is shown along with the symmetry indicator ratio $(\delta_G - \delta_H)/\delta_F$. The structured ratio of value 1.3 + 0.3 indicates that the lower band is *not* an allowed naphthalene-like transition; the ratio value near 0 in the higher band indicates an excited state of species A_g of group D_{2h} (a naphthalene-like state of total symmetry). This state is the third excited singlet state of naphthalene; it is completely hidden to one-photon spectroscopy by the surrounding one-photon states. It lies lower than the best predictions by about 4000 cm^{-1}. The spectra of δ_F, δ_G, and δ_H are given individually in ref 4b.

these together, one might in principle detect a δ as small as 10^{-4} maria by the direct, absolute method.

In the indirect, relative method (Figure 5), in which only a single strong beam is used, the limit of detectability is much lower. Let us assume that quantum yield of fluorescence and detection efficiency are such that we need 10^4 excitations in 10 nsec in order to see a fluorescence pulse. Then still assuming $\delta = 1$ maria, and taking $l = 1$ cm, $C = 10^{20}$ molecule cm^{-3} (or 0.17 M), $A = 10^{-2}$ cm^2, we arrive through eq 8 at a required optical power P of only 10^{20} photon sec^{-1}, or 40 W in the green. (For this case we have set $P_1 = P_2 = P$). Any tunable pulsed laser can achieve this power quite easily. Using the 40-kW pulsed laser of the previous example would permit a δ of 10^{-6} maria to be detected. One might extend this by several orders of magnitude by improving the detector or increasing the laser intensity. The latter is particularly effective, considering the quadratic dependence on P.

Without going into details, it should be recognized that the accuracy and reproducibility of both methods depend on having a pulsed laser whose beam is a smooth, single peaked function in both space and time. Further, its spatial characteristics must be en-
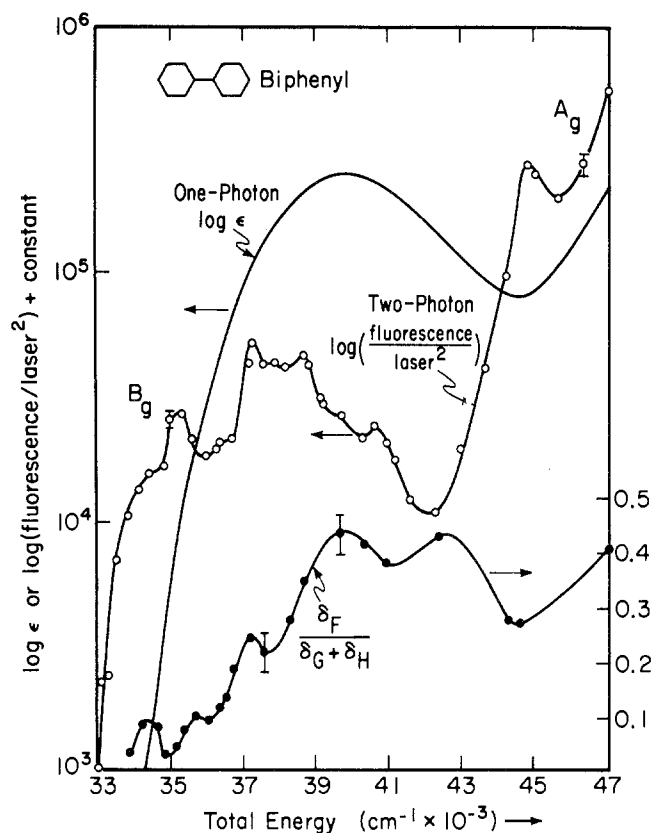

Figure 8 Two-photon spectrum of biphenyl dissolved in cyclohexane (nearly saturated solution, room temperature), by the fluorescence method.[6c] The fluorescence begins well before the onset of one-photon states and has indicator ratio $\delta_F/(\delta_G + \delta_H)$ near zero, pointing to a B_g excited state as the lowest excited singlet. One-photon work indicated a "hidden" state near the bottom of the manifold, but could not assign the symmetry. The strong fluorescence at higher energy has polarization characteristics consistent with A_g symmetry. This ordering of states is predicted only by a theory that treats electron correlation explicitly.[9]

tirely reproducible from shot to shot. The only type of laser that meets this criterion is a single-mode laser, selected for single longitudinal mode as well as for single transverse mode. Most of the experimental difficulties in the pioneering period 1961–1968 can be traced to the fact that such lasers did not exist then in two-photon laboratories.

This insistence on high quality laser beams can be somewhat relaxed in the fluorescence method if one is content to measure only the relative δ of different polarization cases. This is explained in the caption of Figure 5.

Some Results

In Figures 6, 7, and 8 we show exemplary two-photon spectra which illustrate the methods discussed above. Figure 6 is a crystal spectrum, Figure 7 is a complete polarization study of a liquid, and Figure 8 is from a fluorescence study of a solution. Each one presents information which is hidden to one-photon spectroscopy, or settles a question that was unanswerable by one-photon methods. These points are explained in the captions.[9]

The literature of two-photon spectroscopy is still small, but it is steadily growing. It has been reviewed several times already,[10] and will be reviewed

(9) J. Dancz, Ph.D. Thesis, California, Berkeley, 1970.
(10) (a) W. L. Peticolas, *Annu. Rev. Phys. Chem.*, 18, (1967); (b) H. Mahr in "Physics of Color Centers," H. B. Fowler, Ed., Academic Press,

again shortly by Mahr.[11] We feel sure that the fundamental importance of the questions attacked by this method, and the growing availability of tunable single mode lasers which make it practical, will com-

New York, N. Y., 1968; (c) J. M. Worlock in "Laser Handbook," F. T. Arrechi, Ed., North-Holland Publishing Co., Amsterdam, 1972.

(11) H. Mahr in "Treatise in Quantum Electronics," H. Rabin and C. L. Tang, Ed., Academic Press, New York, N.Y., in press.

bine to make two-photon spectroscopy increasingly useful for finding and describing the geometrically hidden excited states of molecules.

Mercury-Sensitized Luminescence

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Chemical processes initiated by reactions of excited mercury atoms have been studied for many years, and several reviews are available.[1]

Much less attention has been given to the luminescent processes which form the subject of this Account, even though such processes were among the first reactions of excited atoms to be investigated. Thus in 1923 Cario and Franck[2] reported the observation of sensitized fluorescence of thallium when a mixture of thallium and mercury vapors was irradiated with the mercury 253.7-nm resonance line, and a short time later Wood and Gaviola[3] and Mitchell and Dickinson[4] described structureless emission bands which they observed during 253.7-nm irradiation of mixtures of mercury vapor with water and with ammonia. In 1928 Oldenberg[5] described emission bands arising from short-lived excited complexes (excimers) of excited mercury atoms with rare gase atoms; analogous emission continua associated with excimers of formula Hg_2 were first reported in 1913.[6]

Current interest in the luminescent reactions of excited atoms is connected with the possible importance of luminescence as an alternative to photosensitized decomposition in systems where the quantum yield for decomposition is low,[7] and with interest in properties such as radiative lifetimes, reactivities, and decomposition modes of the excimers themselves. A subsidiary source of interest is the possibility that excimers having repulsive ground states might form the basis of new ultraviolet laser systems.

A portion of the energy level diagram for atomic mercury is shown in Figure 1. Atoms in the $^3P_1$ state are readily produced by irradiating room-temperature mercury vapor with the 253.7-nm resonance line from a low-pressure mercury lamp. From the $^3P_1$ level an atom can return spontaneously to the

ground $^1S_0$ state, emitting 253.7-nm fluorescence, with a rate constant of $9 \times 10^6 \, sec^{-1}$.

Alternatively the excited atom may undergo a bimolecular collision, which can lead to quenching to either the ground state or to the metastable 6^3P_0 state or can result in compound formation. Certain quenchers, notably N_2 and CO, are particularly effective at promoting spin–orbit relaxation to the $^3P_0$ level by processes such as

$$Hg(^3P_1) + CO(v = 0) \longrightarrow Hg(^3P_0) + CO(v = 1) \qquad (1)$$
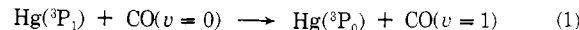
If the exciting radiation is not filtered to isolate the 253.7-nm line, the $^3P_2$ level may also become populated to a significant extent[8] as a result of absorption of 404.7-nm radiation ($7^3S_1 \leftarrow 6^3P_0$) by metastable $^3P_0$ atoms, followed by fluorescence at 546.1 nm ($7^3S_1 \rightarrow 6^3P_2$).

The work to be described has been concerned with reactions of mercury atoms in the 6^3P_1 and 6^3P_0 states, as studied by emission spectroscopy. Reaction rates and excimer lifetimes have been determined by rotating sector or phase-shift studies of modulated excimer luminescence.[9]

Reactions in the Mercury–Ammonia System

The emission bands observed during 253.7-nm irradiation of mixtures of mercury vapor with NH_3 and ND_3 are shown in Figure 2. The bands show no detectable fine structure at a resolution of 0.02 nm, and are believed to be perfectly continuous. An interesting feature of the emission is that its intensity is only very slightly reduced by the addition of a large excess of NH_3 or ND_3.

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(1) R. J. Cvetanovic, *Progr. React. Kinet.* 2, 39 (1964); J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(2) G. Cario and J. Franck, *Z. Physik,* 17, 202 (1923).

(3) R. W. Wood, *Phil. Mag.,* 50, 774 (1925); 4, 466 (1927); E. Gaviola and R. W. Wood, *ibid.,* 6, 1191 (1928).

(4) A. C. G. Mitchell and R. G. Dickinson, *J. Amer. Chem. Soc.,* 49, 1478 (1927).

(5) O. Oldenberg, *Z. Physik,* 47, 184 (1928); 51, 605 (1928); 55, 1 (1929).

(6) F. S. Phillips, *Proc. Roy. Soc., Ser. A,* 89, 39 (1913).

(7) S. Penzes, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.,* 45, 2322 (1966).

(8) H. E. Hunziker, *IBM J. Res. Develop.,* 15, 10 (1971).

(9) L. F. Phillips, *Progr. React. Kinet.,* 7, Part 2, 83 (1973).