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Two-photon absorption by rotating diatomic molecules†

by R. G. BRAY and R. M. HOCHSTRASSER

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Explicit forms for the two-photon absorption cross section in linearly and circularly polarized light for rotating diatomic molecules have been developed. The ratio \( \sigma_{ll}/\sigma_{cc} \) of the cross sections for individual rotational transitions is precisely two-thirds for all branches of \( \Delta \Omega = 0, \pm 1, \pm 2 \) transitions except for the unique case—the Q branch of a \( \Delta \Omega = 0 \) transition. In the latter case the ratio becomes \( J \)-dependent and may range from infinity to 4/1 (for high \( J \)) for different relative contributions to the absorption cross section of intermediate states having either the same or different electronic symmetry. These contributions are thus experimentally accessible in this favourable situation.

1. INTRODUCTION

The recent advances in laser technology render feasible many experiments in spectroscopy that were hitherto extremely cumbersome. In the early days of Raman scattering experiments it was clearly quite difficult to obtain well-resolved scattering spectra from gases at moderate pressures. Thus the theoretical developments such as the calculations by Placzek and Teller [1] on Raman intensities and the manner in which these depend on rotational quantum numbers were not often used systematically in experiments. The availability of dye lasers with tunability and high resolution capability has recently provided the means of examining rovibronic two-photon spectra of molecules in dilute gases [2, 3]. These excitation spectra are often much easier to obtain than rotational Raman spectra, and of course the Placzek–Teller approach is applicable also to certain special cases of two-photon absorption and emission.

Of great interest in spectroscopy is the assignment of states and of quantum numbers to states. In non-linear two-photon processes this can often be done in principle by polarization measurements [4] because the successive absorption of two photons, whose relative polarization may be chosen by the experimenter, is involved. Essentially the system is prepared by the first photon in a non-stationary state that can be caused to undergo transitions to the final state by photons having only certain polarizations. This is analogous to controlling the scattered (second) photon in the linear process of Raman scattering by introducing a polarizer to analyse the emitted light. Thus by choosing two different

† This research was supported by a P.H.S. grant, GM12592 and in part by the NSF/MRL programme at the University of Pennsylvania.
combinations of polarizations—various useful possibilities were outlined by Monson and McLain [5]—it is possible, even in a dilute gas, to make state and quantum number assignments based on polarization measurements [6, 7].

In this paper the case of diatomic molecules is mainly considered. Rotationally resolved spectra for two diatomics nitric oxide [3] and iodine [8] already exist. There appears to be no reason why two-photon spectra at moderately high resolution should not be obtainable for many diatomic molecules and free radicals whether by the fluorescence [2] or the recent photoionization technique [8, 9]. In what follows we refer mainly to a two-photon absorption experiment but a detailed analysis of other processes such as the electronic Raman effect will automatically require the results in the form they are given here.

2. THE TWO-PHOTON ABSORPTION EXPERIMENT

A convenient method for obtaining moderately well-resolved two-photon spectroscopy—e.g. Doppler limited spectra in which hyperfine structure is not resolved—involves using two photons travelling in the same direction and from the same laser beam. For isotropic gas spectra this means that both photons in the two-photon process must have the same polarization. (Of course this is not a necessary restriction for anisotropic solids using the same technique.) With conventional dye lasers it is easier to have output at a single frequency, and although this is not a necessary condition for two-photon absorption it is nevertheless a convenient one both from the theoretical and experimental standpoints. In what follows we will usually assume that the two photons have the same energy. Clearly when the two photons have different energies the ordering of coupling of the photons with the molecule will influence the two-photon absorption cross section and anisotropy. Such experiments, and the theory of them for rotational states, are therefore an important future problem. Far-off resonance, the presence of two photons having different frequencies (the sum of which matches a one-photon resonance) implies that the amplitude consists of two different contributions that may interfere, while if one photon is close enough to a resonance the two-photon process for an ensemble of molecules ultimately contains a consecutive component and the ordering becomes crucial. Neglecting ordering difficulties, and when the coupling virtual states are off-resonance by precisely the photon energy, the two-photon absorption intensity is proportional to the quantity

\[ \sigma_{ss}(0|f) = \left| \sum_i \frac{\langle f | \epsilon_z \epsilon_z | i \rangle \langle i | \epsilon_z \epsilon_z | 0 \rangle}{\Delta \varepsilon_0 - \hbar \omega + i \Gamma_i/2} \right|^2 , \]

where the two-photon transition occurs from an initial rovibronic state \( |0\rangle \) to a final rovibronic state \( |f\rangle \) by simultaneous absorption of two photons each having energy \( \hbar \omega \) and polarization component \( \epsilon_z \) in direction \( \alpha \) of a laboratory-fixed axis system. The intermediate rovibronic states \( |i\rangle \) are separated from the initial state by \( \Delta \varepsilon_0 \) and from the laser photon energy by \( (\Delta \varepsilon_0 - \hbar \omega) \). \( \Gamma_i \) is the total homogeneous width (radiative and non-radiative) of the intermediate state. A convenient experimental and theoretical quantity is \( \sigma_{ss}(0|f) / \sigma_{ll}(0|f) \) corresponding to the ratio of the two-photon cross sections in circularly (c) and linearly (l) polarized light.
3. Calculation of the Transition Amplitudes

3.1. Basis states and transition amplitudes

Under the experimental conditions described above the details of the energies of the rovibronic levels of a particular intermediate state \(|\tilde{f}\rangle\) need not be considered explicitly in the denominator of the transition amplitude. Thus \(\Delta \varepsilon_{\text{ini}}\) can be chosen to represent an average energy separation between the appropriate rovibronic levels of the initial and intermediate states. Under these circumstances the amplitude in (1) separates into a small number (usually two or three) of terms, each of which factors into a product of electronic and rovibronic parts. This is because the rotational selection rules and amplitudes are the same for transitions to all the virtual electronic states of a particular symmetry type.

Following Hougen [10] we write the molecular states in the basis \(|\Lambda S \Sigma ; \Omega J M\rangle\), where the non-rotating molecule basis involves \(\Lambda\) (orbital angular momentum projection on internuclear axis), \(S\) (total spin) and \(\Sigma\) (the electron spin projection); the rotating molecule part involves the quantum numbers \(\Omega\) (projection of the total angular momentum), \(J\) (the total angular momentum) and \(M\) (the projection of the total angular momentum onto a space-fixed axis \(Z\)). These basis functions can be written as \(|evr\rangle = |ev\rangle |r\rangle\), where \(e, v,\) and \(r\) symbolize electron, vibration and rotation respectively.

The laboratory-fixed components of the dipole operator \(r_{\alpha}\) can be written as

\[
r_{\alpha} = \sum_{s} G_{\alpha s} r_{s},
\]

where the \(G_{\alpha s}\) are the elements of the direction cosine matrix describing the relative orientation of molecular (\(s\)) and space-fixed (\(\alpha\)) axes. The matrix of \(G_{\alpha s}\) in the rotating basis is available from many sources including reference [10]. For the linearly polarized light experiment the operator \(r_{z}\) is used, and most conveniently in the form

\[
r_{z} = 2^{-1/2}[G_{Z}^{+}r^{-} + G_{Z}^{-}r^{+}] + G_{Z}^{z}r_{z},
\]

where \(G_{Z}^{\pm} = (G_{Zx} \pm iG_{Zy})\) and \(r^{\pm} = 2^{-1/2}(r_{x} \pm ir_{y})\). For the circularly polarized light experiment the appropriate dipole operator is

\[
r_{c} = 2^{-1/2}(r_{x} + ir_{y}) = \frac{1}{2}[G_{X}^{+} + iG_{Y}^{+}]r^{-} + (G_{X}^{-} + iG_{Y}^{-})r^{+} + r_{z}(G_{Xz} + iG_{Yz}).
\]

The usefulness of these forms for the dipole operator relate to the existence of only certain matrix elements of the molecule-fixed components of \(r\) in the non-rotating basis set; namely the following:

\[
\mu_{\pm} \equiv \langle \Omega \pm 1 |er^{\pm}|\Omega\rangle,
\]

\[
\mu_{\mp} \equiv \langle \Omega |er_{z}|\Omega\rangle.
\]

The two-photon transition amplitude may now be reduced to a sum of terms, each of which is the product of two factors each consisting of an electronic (involving \(\mu_{\pm}\) or \(\mu_{\mp}\)) and rotational (involving matrix elements of \(G\)) part. The first step in the calculation of (1) is to obtain correctly phased values for the matrix elements of \(r_{l}\) and \(r_{c}\), i.e.
<table>
<thead>
<tr>
<th>Polarization</th>
<th>$J' = J + 1$</th>
<th>$J' = J$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Linear</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\times \langle \Omega</td>
<td>\mu_z</td>
<td>\Omega \rangle = \mu$</td>
</tr>
<tr>
<td><strong>Circular</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\times \langle \Omega</td>
<td>\mu_z</td>
<td>\Omega \rangle$</td>
</tr>
<tr>
<td><strong>Linear</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^{-1/2} \langle \Omega + 1</td>
<td>\mu_z + i\mu_y</td>
<td>\Omega \rangle = \mu_+$</td>
</tr>
<tr>
<td>$2^{-1/2} \langle \Omega - 1</td>
<td>\mu_z - i\mu_y</td>
<td>\Omega \rangle = \mu_-$</td>
</tr>
<tr>
<td><strong>Circular</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2^{-1/2} \langle \Omega + 1</td>
<td>\mu_z + i\mu_y</td>
<td>\Omega \rangle$</td>
</tr>
<tr>
<td>$2^{-1/2} \langle \Omega - 1</td>
<td>\mu_z - i\mu_y</td>
<td>\Omega \rangle$</td>
</tr>
</tbody>
</table>

$C_{JJ'}$ | $[16(J + 1)^2(2J + 1)(2J + 3)]^{-1/2}$ | $[4(J + 1)]^{-1}$ |
<table>
<thead>
<tr>
<th>Polarization</th>
<th>( J' = J - 1 )</th>
<th>( \Delta M )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Linear</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \times \langle \Omega</td>
<td>\mu_z</td>
<td>\Omega \rangle = \mu )</td>
</tr>
<tr>
<td><strong>Circular</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \times \langle \Omega</td>
<td>\mu_z</td>
<td>\Omega \rangle )</td>
</tr>
<tr>
<td><strong>Linear</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \times 2^{-1/2} \langle \Omega + 1</td>
<td>\mu_z + i\mu_y</td>
<td>\Omega \rangle = \mu_+ )</td>
</tr>
<tr>
<td>( \times 2^{-1/2} \langle \Omega - 1</td>
<td>\mu_z - i\mu_y</td>
<td>\Omega \rangle = \mu_+ )</td>
</tr>
<tr>
<td><strong>Circular</strong></td>
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<tr>
<td>( \times 2^{-1/2} \langle \Omega + 1</td>
<td>\mu_z + i\mu_y</td>
<td>\Omega \rangle )</td>
</tr>
<tr>
<td>( \times 2^{-1/2} \langle \Omega - 1</td>
<td>\mu_z - i\mu_y</td>
<td>\Omega \rangle )</td>
</tr>
</tbody>
</table>

\[ C_{JJ'} = [16J'(2J - 1)(2J + 1)]^{-1/2} \]

These one-photon amplitudes are given in the basis \( |\Delta \Sigma \rangle ; \Omega JM \rangle \) defined in the text. If for example, the matrix elements for II±-type states or other basis states are needed, the result will be a superposition of amplitudes from this table. The usual line strength factor, \( S \), does not incorporate the orientation average implicit in the squares of our amplitudes; thus to reproduce a standard table of line strength factors it is necessary to square the amplitudes in this table then multiply by 3 or 3/2 for parallel or perpendicular transitions respectively.

The choice of \( \mu_+ = \pm \mu_+ \) (see column 1) is determined by the behaviour of the initial and final states under the symmetry operation \( \sigma_\nu \). When these are both symmetric or both antisymmetric to \( \sigma_\nu \) then \( \mu_+ = \mu_+ \), otherwise \( \mu_+ = -\mu_+ \). For example, for \( \Omega = \Omega^+ \), a \( 1\Sigma^+ \) state, and a \( 1\Pi \) state (\( \Omega = 1 \)) correlating with a united atom state of odd parity [10] we have \( \mu_+ = -\mu_+ \); this example corresponds to the \( 1\Pi_u \leftrightarrow \Sigma_g^+ \) transitions of homonuclear diatomics.

\( C_{JJ'} \) is that portion of the relevant direction cosine matrix elements that is independent of \( \Omega \) and \( M \).

Table 1. One-photon amplitudes \( \langle \Delta ' \Sigma \rangle ; \Omega J'M' | \mu_z | \Delta \Sigma \rangle ; \Omega JM \rangle \).
These are the quantities which if squared would give the one-photon intensity, but the two-photon intensity contains sums of products of them and so they must be carefully phased. The one-photon amplitudes needed for two-photon intensity calculations in the case of $\Omega' \leftrightarrow \Omega$ transitions are given in table 1. In the absence of external fields, when the $M$-levels are not observed separately, the usual one-photon intensities for a particular $\Delta J$ are obtained by evaluating the squared modulus of the appropriate term from table 1 multiplied by $C_{J,J'}$ and the transition dipole factor, and summing over $M$: the result will be independent of which polarization is used, illustrating the isotropy of space. It is always the case that $|\mu_+| = |\mu_-|$ but they may differ in sign depending on the transformation properties of the integrand under reflection in the $\sigma_v$-plane.

### 3.2. Pathways for two-photon absorption

The structure of the two-photon amplitude is very easily seen from diagrams

![Diagram showing possible intermediate states and one-photon transition moments](image)

Figure 1. Structure of the two-photon transition amplitude for a diatomic molecule showing possible intermediate states and one-photon transition moments. The prime notation is that used in tables 2 and 3. For the one-photon steps the usual rules $\Sigma \leftrightarrow \Sigma^*$, $\sigma \leftrightarrow \sigma^*$, etc. apply.
Two-photon absorption

Figure 2. Structure of the two-photon transition amplitude for a diatomic molecule showing the detailed J-dependence of particular transitions. A $\Pi_\pm$ level is $(\Pi_1 \pm \Pi_{-1})$, and the detailed rotational selection rules depend on the symmetry of $\Pi_\pm$ to the operation $\sigma_v$. $\Pi_+$ is chosen to be an even (so $\Pi_-$ is an odd) function of $\sigma_v$. For the case $^1\Sigma^+ \rightarrow ^1\Sigma^-$ these same intermediate states could be used but the + and - designations on $\Pi$ would need to be interchanged.

of the type shown in figure 1. The intermediate states of a given type are shown as dashed lines (one line for each group of electronic states that can enter into the process) and the possible transitions are drawn in using well-known one-photon selection rules. More detailed diagrams displaying the $J$-changes involved in the processes are helpful in organizing the various terms that contribute to the amplitude (e.g. see figure 2). Thus from figure 2 (a) it is immediately obvious that the Q-branch two-photon transition amplitude contains five terms, the O and S branch amplitudes each have two terms and that a $^1\Sigma^+ \rightarrow ^1\Sigma^+$ transition can display no P and R branches. Figures 2 (b) and (c) give the detailed diagram for a $\Pi \rightarrow \Sigma$ transition: In this case the P and R-branch amplitudes appear through the $\Pi_- \rightarrow \Sigma^+$ part for our parity choices, and they each consist of three terms.

These diagrams (figures 1 and 2) and the general cases from the tables signify in a simple pictorial fashion the possible quantum states that can in principle interact with the light field. In practice the light drives the system into a non-stationary state that consists of a superposition of many levels, each contributing to an extent that depends on its transition moment and energy denominator.
However, all states of a given \( \Omega \) for a given united atom parentage in the intermediate state have the same rotational selection rules with respect to both of the photons involved in the process. Thus in what follows we will use the symbols \( \mu_\pm \) to represent the collective effect of all these one photon transition moments and energy denominators that give rise to parallel or perpendicular transitions. These parameters \( |\mu_+| \) and \( |\mu_-| \) can be measured experimentally from gas-phase spectra in certain cases, so it should be of some interest to make numerical calculations of them from model molecular wavefunctions.

3.3. Explicit forms for the two-photon transition intensity

With the aid of the detailed diagrams of figure 2 and the properly phased amplitudes from table 1 it is straightforward to find the appropriate superpositions that occur in the two-photon transition moment for any rotational branch. The basis set used in table 1 is always suitable to describe the intermediate states since they always occur as a superposition of a complete set of components. On the other hand, the initial and final states have definite wavefunctions dependent on the types of interactions occurring in the molecule. The values of \( \sigma_{11} \) and \( \sigma_{\pi} \) are then obtained (in the absence of external fields) by squaring the superposition appropriate to the branch under consideration and summing over \( M \). The \( M \) sums were achieved using the following well-known relationships:

\[
\sum_{J} M^{2} = \frac{1}{2} J(J+1)(2J+1),
\]

\[
\sum_{J} M^{4} = \frac{3}{16} J(J+1)(2J+1)(3J^{2}+3J-1).
\]

The results are presented in tables 2 and 3 in terms of the quantum numbers \( J \) and \( \Omega \) for the various possible transitions. Included in table 2 are \( \Sigma \leftrightarrow \Pi \), \( \Sigma \leftrightarrow \Delta \), \( \Pi \leftrightarrow \Delta \), etc. transitions, while table 3 deals specifically with the more revealing cases of \( \Sigma \leftrightarrow \Sigma \), \( \Pi \leftrightarrow \Pi \), etc. transitions. For cases where the initial and final states of the two-photon process have the same set of quantum numbers \( (J, \Omega) \) the trace scattering through \( \mu_{\pi}^{2} \) (see table 3) causes an increase in the absorption intensity for linear compared with circularly polarized light. In all other cases—that is whenever the \( J \) or \( \Omega \) quantum numbers are different in the combining states—the absorption of circularly polarized light is always precisely \( \frac{9}{8} \) that of linearly polarized light. This latter result was already experimentally verified for a \( \Sigma \leftrightarrow \Pi \) transition of nitric oxide, where the ratio \( \sigma_{\pi}/\sigma_{11} \) was \( \frac{3}{2} \) for all rotational branches as expected from the present theory [7]. The unique case occurs for the Q-branch of a \( \Omega \leftrightarrow \Omega \) transition in which case the polarization ratio is

\[
(\sigma_{11}/\sigma_{\pi}) = \frac{10J(J+1)(2J+3)(2J-1)(\mu_{+}^{2}/\mu_{-}^{2})}{3[2J(J+1)-3\Omega^{2}]} + \frac{9}{8}.
\]

† This statement will also be correct for symmetric tops when the transition involves no change in \( J \) and \( K \) (the projection of the angular momentum on the top axis). For symmetric tops this situation arises only for \( \Delta K = 0 \), \( \Delta J = 0 \) transitions, or Q branches of transitions having the same vibronic symmetry in both electronic states.
When considering the intensity of transitions between two states having different electronic angular momentum it is frequently necessary to consider contributions to the amplitude terminating on or originating from | − Ω⟩ as well as the |Ω⟩ component states. The transition dipole factor would then consist of a sum of these contributions taken in such manner as demanded by the interactions within the molecule. For example if the distinguishable states are $2^{-1/2}[|Ω⟩ ± |−Ω⟩]$ the transition dipole factors in the first column would be $|μ_+μ_- + μ'_-μ'_+|2$ for P and R branches, and those in the second column would be $|μ_−μ'_+ ± μ_+μ'_-|2$ for O, Q and S branches. The intensities for circularly polarized light are obtained by multiplying the entries in this table by 3/2.

Table 2. Two-photon transition strengths for diatomic molecule transitions in linearly polarized light.
<table>
<thead>
<tr>
<th>Branch</th>
<th>Circular polarization</th>
<th>Linear polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>O branch</td>
<td>(\frac{(J^2 - \Omega^2)(J + 1)^2 - \Omega^2)}{20J(J-1)(2J-1)})</td>
<td>(Same as circular) (\times \frac{3}{2})</td>
</tr>
<tr>
<td>P branch</td>
<td>(\frac{\Omega^2(J^2 - \Omega^2)}{10J(J+1)(J-1)})</td>
<td>(Same as circular) (\times \frac{3}{2})</td>
</tr>
<tr>
<td>Q branch</td>
<td>(\frac{(2J+1)(J(J+1)-3\Omega^2)^2}{30J(J+1)(2J+3)(2J-1)})</td>
<td>(\frac{(2J+1)[J(J+1)-3\Omega^2]^2}{9} \mu^2 + \frac{(2J+1)(J(J+1)-3\Omega^2)^2}{45J(J+1)(2J-1)(2J+3)} \mu s^2)</td>
</tr>
<tr>
<td>R branch</td>
<td>(\frac{\Omega^2(J+1)^2 - \Omega^2}{10J(J+1)(J+2)})</td>
<td>(Same as circular) (\times \frac{3}{2})</td>
</tr>
<tr>
<td>S branch</td>
<td>(\frac{(J+1)^2 - \Omega^2)(J+2)^2 - \Omega^2}{20(J+1)(2J+3)})</td>
<td>(Same as circular) (\times \frac{3}{2})</td>
</tr>
</tbody>
</table>

Transition dipole factor:

\[ \otimes |2\mu_+ \mu_\perp - \mu_+ \mu_\perp - \mu_\perp \mu_+ |^2 = \mu S^2 \]

\[ \mu T^2 = |\mu_+ \mu_\perp + \mu_+ \mu_\perp + \mu_\perp \mu_+|^2 \]

Table 3. Two-photon transition strengths for diatomic molecule transitions of the type \(|\Omega_\perp\Omega^*|\Omega_\perp\rangle\).
Two-photon absorption

It follows that the ratio $\mu_1^2/\mu_2^2$ can be measured simply by obtaining $\sigma_{\|}/\sigma_{\perp}$ for the Q-branches of diatomic molecule rovibronic spectra. It is useful to note that for high $J$ the polarization ratio (9) becomes

$$\left(\frac{\sigma_{\|}}{\sigma_{\perp}}\right) = \frac{3}{2}\left[1 + 20\left(\frac{\mu_1^2}{\mu_2^2}\right)\right]$$

and this ranges from infinity (i.e. no absorption of circularly polarized light) for the case $\mu_2^2=0$, to 14 : 1 when only perpendicular transitions are involved, to 4 : 1 when there are only parallel transitions. If the contributions from all the rotational branches originating from a particular $J$ are summed for the $\Omega \leftrightarrow \Omega$ case one obtains

$$\left(\frac{\sigma_{\|}}{\sigma_{\perp}}\right) = \frac{3}{2}\left[1 + 5\left(\frac{\mu_1^2}{\mu_2^2}\right)\right]$$

and substitution of $r = (\mu_1^2/\mu_2^2)$ yields

$$\left(\frac{\sigma_{\|}}{\sigma_{\perp}}\right) = \frac{3}{2}\left(8r^2 + 4r + 3\right)/(2r - 1)^2.$$  

This is the formula developed by McLain et al. [5, 6] in relation to the two-photon absorption of molecules tumbling in liquids. Formula (10) is the one that should be used for interpreting the Q-branch polarization ratio, and not (12) as suggested by Friedrich and McLain [6]. If the symmetric scattering is strong (i.e. $\mu_1^2 \gg \mu_2^2$), then the polarization ratio using (10) will be four times larger than that calculated from the relations (11) or (12) for tumbling molecules.

Some other general features of the results are as follows: (a) P and R branches do not occur in $\Sigma \leftrightarrow \Sigma$ transitions; (b) P and R branches for $\Delta \Lambda = 0$, $\Omega \neq 0$ transitions decrease in line strength with increasing $J$ without going through a maximum; (c) for $\Omega \pm 1 \leftrightarrow \Omega$ transitions displays a Q branch whose line strength decreases rapidly with increasing $J$, whereas other transitions increase in line strength linearly with $J$; (d) $\Omega \pm 1 \leftrightarrow \Omega$ transitions display a Q branch whose line strength decreases rapidly with increasing $J$; (e) $\Sigma \leftrightarrow \Sigma$ transitions cannot occur in two-photon absorption when the two photons have the same frequency: This is readily seen as a result of the absence of $\Sigma^-$ from the symmetric direct product $\Pi \otimes \Pi$. When the two-photons have different frequency it will be possible to observe $\Sigma^+ \rightarrow \Sigma^-$ transitions in two-photon absorption.

4. Application

There are no available two-photon absorption intensity measurements for diatomics but we have made some two-photon excitation intensity measurements on NO. The experimental results compared with the present theory for two-photon absorption are shown in figure 3. It is apparent that they do not agree for the $O_{1\alpha}$-branch points given in the figure. The data points refer to the range of pressures 48 torr to 20 mtorr. The lowest of these pressures, at which the deviations are greatest, is well below that claimed by Broida and Carrington.

† Although there are no examples yet of two-photon spectra of diatomics both in the gaseous and liquid phase, we do have one such example for the symmetric top benzene. In hexane solution at 300 K the two-photon absorption polarization for the $14_{1\alpha}1_{n}$ progression was found by us to be less than 5, whereas in the gas phase the polarization of what is probably mainly the Q branch was found [6, 7] to be greater than 20. For a symmetric top $A \leftrightarrow A$ transition having undispersed $K$ structure the polarization ratio in the gas would be 5 times that found for molecules tumbling in solution.
Figure 3. Comparison of theoretical two-photon absorption intensities with experimental excitation intensities for rotational transitions (O12 branch) of the nitric oxide γ (0, 0) band. The excitation spectra were obtained as before (reference [3]), using a Molectron UV 1000, DL 200 pulsed dye laser system having ca. 1 cm⁻¹ (f.w.h.m.) linewidth. The experimental points represent integrated intensities, the average of three spectra (48 and 0.2 torr) or one signal averaged (16 ×) spectrum (20 mtorr). All intensities are arbitrarily normalized to the relative theoretical value at J=6 for one signal averaged spectrum (20 mtorr).

[11] to represent the limiting pressure for collisionally induced rotational relaxation. At 20 mtorr the Hanle effect widths measured by German et al. [12] are within a few per cent of the values extrapolated to zero pressure†. The theoretical curve of figure 3 is drawn for a transition between a limiting case (a) state to a state having spectrally unresolved rho-doubling. The deviation of the excitation spectrum relative intensities shown in figure 3 from those calculated is still under study but we bring it out here to emphasize the importance of making comparisons of results of indirect measurement techniques with theoretical expectations for the assumed processes. In the present instance potentially fluorescent states reached by two photon absorption may interact with other photons instead of emitting.

5. SUMMARY

We have presented the basic theory of the selection rules for two-photon absorption in rotating molecules. While the actual calculation of the intensities for two-photon transitions is simplest for spherical tops and diatomics, the

† mtorr ≈ 1.33 Pa.
Two-photon absorption

Anisotropic features of the results are correct also for symmetric tops with \( \Omega \rightarrow \Omega, \Omega \pm 1, \Omega \pm 2 \) corresponding to \( \Delta K = 0, \Delta K = \pm 1 \) and \( \Delta K = \pm 2 \) transitions, the \( K \) selection rules being determined by the vibronic species of the combining states. These results are quite similar to those in the classic paper by Placzek and Teller [1]. Since these authors dealt with the vibrational Raman effect the initial and final electronic states were always the same, whereas in two-photon absorption they are frequently different.

The two-photon cross section is extremely small compared with a one-photon process, so the two-photon techniques that are in the process of development are usually indirect. The techniques of using a high resolution tunable dye laser and detecting the fluorescence emission following two-photon absorption was the first to be used for rovibronic two-photon spectra [2, 3]. More recently a novel method capable of rovibronic resolution using multiphoton ionization has been introduced [8, 9]. There are other possibilities for detecting two-photon absorption such as by the sensitive optoacoustic effect [13]. All of these approaches produce excitation spectra rather than absorption spectra. For this reason it is important to have an accurate theoretical notion of the actual two-photon intensity distribution. This point is evidenced herein with reference to the \( O_{12} \) branch of the NO \( \gamma \)-bands in two-photon excitation.

A main result of this paper is a more detailed description of a point we have made earlier [7] regarding the polarization of two-photon transitions. Just as is the case for atoms, when the initial and final states of a two-photon transition in a molecule are identical—excluding the factor specifying the orientation of the molecule in the laboratory—then the absorption of linearly polarized light is enhanced over circularly polarized light. For example, \( S \rightarrow S \) transitions in atoms do not occur in circularly polarized light; \( Q \) branches of diatomics display the anisotropy shown here; \( Q \) branches for \( \Delta K = 0 \) transitions between states having the same total vibronic symmetry may also display structurally useful anisotropies.

Many of the results of this paper can be obtained from formulae in Placzek and Teller [1] by re-interpreting quantum number designations, because the results are after all a consequence of symmetry, but we hope that the notation [10] used here will facilitate and encourage the use of these results in the fast-growing field of two-photon spectroscopy.

References