Rotational Line Strengths in Two- and Three-Photon Transitions in Diatomic Molecules

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Rotational line intensity factors are calculated for two- and three-photon excitation of diatomic molecules belonging to Hund's case (a) and intermediate (a)-(b) coupling schemes. The intensity factors compare well with experimentally measured normalized line intensities for two-photon transitions in the Lyman-Birge-Hopfield system of N₂, the γ-bands of NO and the fourth-positive system of CO and for three-photon excitation of the fourth-positive system of CO.

I. INTRODUCTION

The development of tunable dye lasers has led to the development of two-photon excitation as a powerful tool for the spectroscopic study of atoms and molecules. Bray et al. (1) first demonstrated that this method can be of good advantage for inducing electronic transitions in dilute diatomic gases. They were able to resolve the rotational structure of the \( \text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi \) transition in NO, despite the rather large bandwidth of their exciting laser. With the construction of intense, narrow band dye laser systems two-photon excited molecular spectra have been studied under high resolution (Lombardi et al. (2); Wallenstein and Zacharias (3)). In addition Faisal et al. (4) were able to observe the simultaneous molecular absorption of three photons. Intense tunable ultraviolet laser light allows the use of two-photon absorption for the excitation of single rotational lines of electronic transitions located in the vacuum ultraviolet (Filseth et al. (5)).

The relative line intensities in two- and three-photon spectra are different from those known for one-photon absorption. Bray and Hochstrasser (6) calculated the line intensities of two-photon transitions in diatomic molecules between states belonging to Hund's case (a) (7). In the present paper we derive the rotational line intensity factors for two- and three-photon excitation of doublet states belonging to Hund's cases (a) or (b) or to the intermediate (a)-(b) coupling case. Thus, the expressions presented will describe the rotational intensity distributions of many important two- and three-photon electronic transitions in diatomic molecules.

The calculated rotational line intensity factors are compared with experimental values, evaluated from line intensities, measured from two-photon excitation spectra of the Lyman–Birge–Hopfield system of N₂, the fourth-positive system of CO, and the γ-bands of NO. The results for three-photon transitions are compared with measurements on three-photon excitation in the fourth-positive system of CO.

II. CALCULATION OF THE TRANSITION RATES

In this section expressions for the rotational line intensity factors are developed for two- and three-photon excitation of singlet and doublet states in diatomic molecules, which belong to Hund’s case (a), (b) or the intermediate (a)–(b) coupling case. Here the results of Bray and Hochstrasser (6) are arrived at by a slightly different approach. Special attention is paid to the role played by the various types of intermediate virtual states and to estimation of errors caused by simplifying assumptions.

II.1. Two-Photon Absorption

The transition rate $K$ for two-photon absorption is given in lowest order perturbation theory by

$$
\hbar K = \sum_i \frac{\langle \psi_f | \mathbf{M} \cdot \mathbf{E} | \psi_i \rangle \langle \psi_i | \mathbf{M} \cdot \mathbf{E} | \psi_g \rangle}{\hbar \omega_{ig} - \hbar \omega}.
$$

where $\psi_i$ and $\psi_f$ are the initial and final states, respectively, $\omega$ is the photon frequency, and $\hbar \omega_{ig}$ the energy difference between the $i$th and $g$th quantum state. The operators are the inner products of the molecular dipole moment, $\mathbf{M}$, and $\mathbf{E}$, the electric field of the exciting light.

The sum is taken over all intermediate states of the molecule and each matrix element represents a virtual rotational, vibrational, or electronic transition. Further, in this paper, the initial and final states are assumed to belong to different electronic levels (Merchant and Isenor (9)). Therefore the sum in Eq. (1) can be separated into five terms, i.e.,

$$
\hbar K = \left| \sum_{i=1}^{5} K_i \right|^2
$$

where the components, $K_i$ correspond to the five sets of transitions shown in Fig. 1 and are given by the following expressions:

(a) The intermediate state is in a different electronic state than the initial and final states,

$$
K_1 = \sum_{q \neq q_0 \neq q_0} \frac{\langle q_i v_i J_f | \mathbf{M} \cdot \mathbf{E} | q_i v_i J_i \rangle \langle q_i v_i J_i | \mathbf{M} \cdot \mathbf{E} | q_g v_g J_g \rangle}{\hbar (\omega_{ig} - \omega)}.
$$

(b) The intermediate state is in the initial electronic state but in a different vibrational level than the initial state.

$$
K_2 = \sum_{v \neq v_0} \frac{\langle q_i v_i J_f | \mathbf{M} \cdot \mathbf{E} | q_i v_i J_i \rangle \langle q_i v_i J_i | \mathbf{M} \cdot \mathbf{E} | q_g v_g J_g \rangle}{\hbar (\omega_{ig} - \omega)}.
$$
The intermediate state is in the final electronic state but in a different vibrational level than the final state,

\[ K_3 = \sum_{q \neq q_i} \frac{\langle q_f v_f J_f | M \cdot E | q_v v_i J_i \rangle \langle q_i v_i J_i | M \cdot E | q_v v_f J_f \rangle}{\hbar(\omega_{q_i} - \omega)} . \]  

The intermediate state is in the same electronic and vibrational state as the initial state but the rotational quantum state is different,

\[ K_4 = \sum_{J \neq J_i} \frac{\langle q_f v_f J_f | M \cdot E | q_v v_i J_i \rangle \langle q_i v_i J_i | M \cdot E | q_v v_f J_f \rangle}{\hbar(\omega_{j_i} - \omega)} . \]  

The intermediate state is in the same electronic and vibrational state as the final state but the rotational quantum number is different,

\[ K_5 = \sum_{J \neq J_f} \frac{\langle q_f v_f J_f | M \cdot E | q_v v_f J_f \rangle \langle q_i v_i J_i | M \cdot E | q_v v_f J_f \rangle}{\hbar(\omega_{j_i} - \omega)} . \]  

In these equations the different electronic, vibrational, and rotational quantum numbers are represented by \( q, v, \) and \( J, \) respectively. \( K_5 \) is the sum of products of two transition dipole moments connecting different electronic states (Fig. 1a). \( K_2 \) is the sum of products of one transition dipole matrix element (TME) between vibrational levels of the initial electronic state and a TME connecting the excited vibrational level with the final electronic state (Fig. 1b). \( K_3 \) is similar, except the virtual vibrational transition connects two vibrational levels of the excited elec-
tronic state (Fig. 1c). \( K_4 \) and \( K_5 \) are analogous to \( K_2 \) and \( K_3 \), but instead of a virtual vibrational TME, they have a virtual rotational TME, coupled with an electronic TME (Figs. 1d and 1e).

Selection rules limit the number of nonzero terms in the individual sums. For homonuclear diatomics, sums \( K_2 \) through \( K_5 \) vanish identically because these molecules have no intrinsic dipole moments. If one takes the selection rules applying to each of the TMEs into account the difference between \( J_f \) and \( J_g \) is restricted to \( 0, \pm 1, \) and \( \pm 2 \). Further, it follows, that in \( K_4 \) and \( K_5 \) there can be only two nonzero terms in each sum for a \( Q \) branch two-photon transition, and one for \( O, P, R, \) or \( S \) branch transitions. For all possible values of \( J_g \) there are then only \( 3(2J_g - 1) \) contributions to \( K_4 \) and \( K_5 \).

If diatomic molecules are treated as perfect harmonic oscillators within any given electronic state vibrational transitions would only be allowed for \( \Delta v = \pm 1 \). In this case each of the sums, \( K_2 \) and \( K_3 \) would have six terms for a \( Q \) branch two-photon transition, four for \( P \) or \( R \) transitions, and two for the \( O \) and \( S \) branches. The number of terms in \( K_2 \) would be further reduced by a factor of two if \( v_g = 0 \), and similarly for \( K_3 \) if \( v_g = 0 \). Although diatomic molecules are not perfect harmonic oscillators the intensity of the vibrational \((0,2)\) band is usually only a few percent of the intensity of the \((0,1)\) band, and transitions with \( \Delta v > 2 \) are in most cases vanishingly weak.

Most of the two-photon experiments performed to date involve exciting molecules from the lowest vibrational level of the ground electronic states to a low lying vibrational level of some other electronic state. The harmonic oscillator approximation gives the best results for states with low vibrational quantum numbers. This is illustrated by the measured values of the higher overtone one-photon vibrational transitions given in rows 2, 3, and 4 of Table I for NO and CO, the heteronuclear diatomics that are studied in this paper. Here the transitions with \( \Delta v > 1 \) can be seen to be much smaller than the \( \Delta v = 1 \) vibrational transition. So in these two cases it is justifiable to neglect vibrational TMEs with \( \Delta v > 1 \) in \( K_2 \). While we have no experimental data available, it seems reasonable to assume that the same rule will hold in evaluation of \( K_3 \). However, there is some possibility that there may be exceptions to this. The two-photon excitation of the \( \text{OH} A-X (0,0) 306.4\text{-nm transition} \), for example, might have a significant contribution from \( K_2 \). This is because the vibrational spectrum of OH is rather strong, even for values of \( \Delta v > 7 \). Of particular concern is the fact that the \((5,0)\) vibrational transition is almost resonant with the \( 612.8\text{-nm photons used in the two-photon excitation of the A state. Some rotational lines are exactly resonant, to within the accuracy of the experimental spectral measurements of the two systems. Thus the energy denominator of \( K_2 \) will be significantly smaller than that in all other terms, while the vibrational TME for the \((5,0)\) vibrational transition will be only a few orders of magnitude smaller than a typical electronic TME. If this is the case, one may expect a significant contribution from \( K_2 \) to the two-photon excitation of the \( A \) state of \( \text{OH} \).

In order to estimate the relative importance of the sums in Eqs. (3) it is convenient to sum the equation over all rotational states. This yields the integrated band averages, which may be related to measured and calculated band \( f \) numbers.
There is, of course, no way of knowing the relative phases of the five sums for any intermediate state without a detailed calculation. Therefore the estimates below are for the magnitudes of the various terms. With this understanding $K_2$ and $K_3$ are

$$|K_2| \sim \frac{1}{\hbar \omega} \sum \langle v_f | v_g \pm 1 \rangle \left[ \frac{g_{af} f_{vg}}{\Delta E_{af} \Delta E_{vg} \pm 1} \right]^{1/2} \tag{4a}$$

and

$$|K_3| \sim \frac{1}{\hbar \omega} \sum \langle v_f \pm 1 | v_g \rangle \left[ \frac{g_{af} f_{vf}}{\Delta E_{af} \Delta E_{vf} \pm 1} \right]^{1/2} \tag{4b}$$

$f_{vf}$ and $f_{af}$ are the vibrational and electronic $f$ numbers, respectively. $g_i$ is the degeneracy of the $i$th state. The matrix elements shown are the vibrational overlap integrals. The reader is referred to Michels (10) for definitions of the oscillator strengths. The energy denominators have been approximated by ignoring the rotational and vibrational contributions. It is interesting to note that if the phases of $K_2$ and $K_3$ were the same, they would tend to cancel each other, because the energy denominators in Eqs. (3b) and (3c) have opposite signs and are approximately equal.
TABLE II
Estimation of the Contribution of the Different Sums in Eq. (3) to the Total Two-Photon Transition Rate $K$

<table>
<thead>
<tr>
<th>NO</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^1\Sigma^+$ - $X^1\Sigma^+$</td>
<td>$2.1 \times 10^{-12}$ cm$^2$</td>
<td>$1.0 \times 10^{-13}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>$i = 2^3\Sigma^+$</td>
<td>$3.8 \times 10^{-10}$ cm$^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i = 2^5\Sigma^+$</td>
<td>$1.2 \times 10^{-10}$ cm$^2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO</th>
<th>$k_4$</th>
<th>$k_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^1\Pi$ - $X^1\Sigma^+$</td>
<td>$2.5 \times 10^{-12}$ cm$^2$</td>
<td>$4.4 \times 10^{-14}$ cm$^2$</td>
</tr>
<tr>
<td>$i = 2^3\Sigma^+$</td>
<td>$0.8 \times 10^{-10}$ cm$^2$</td>
<td></td>
</tr>
<tr>
<td>$i = 2^5\Sigma^+$</td>
<td>$1.6 \times 10^{-10}$ cm$^2$</td>
<td></td>
</tr>
</tbody>
</table>

One may similarly estimate the magnitudes of $K_4$ and $K_5$ to be

$$|K_4| \sim \frac{1}{\hbar \omega} d_g \left[ \frac{g_g f_{gf}}{\Delta E_{gf}} \right]^{1/2} \langle v_g | v_f \rangle$$

and

$$|K_5| \sim \frac{1}{\hbar \omega} d_f \left[ \frac{g_g f_{gf}}{\Delta E_{gf}} \right]^{1/2} \langle v_g | v_f \rangle,$$

where $d_f$ and $d_g$ are the intrinsic dipole moments of the initial and final states.

The contribution to $K_1$ from a particular electronic intermediate state is

$$|K_1|_i \sim \frac{\langle v_g | v_f \rangle}{\hbar (\omega_{tg} - \omega)} \left[ \frac{g_g f_{gi} g_i f_{if}}{\Delta E_{gi} \Delta E_{if}} \right]^{1/2}$$

where the vibrational contribution to the energy of the state has been ignored and we have summed over all of the vibrational levels of the intermediate state.

Unfortunately the data necessary to estimate $K_3$ and $K_4$ are not available because of the difficulty of doing the appropriate experiments. It seems reasonable, however, that $K_3$ and $K_4$ will be of the same order of magnitude as $K_2$ and $K_4$, respectively. Table II lists the estimated values of $K_1$, $K_2$, and $K_4$ as calculated from the data in Table I. $K_1$ has been evaluated for two different intermediate electronic states. Since there are many more electronic states it is likely that this value is an underestimate of $K_1$ although there will be some cancellation between terms with different intermediate states because of different phase factors.

Examination of Table II indicates that the contribution from $K_1$ should dominate in the two-photon excitation of the molecular transitions studied in this paper. This is certainly the case for homonuclear diatomics, where the other sums vanish identically and is probably also the case for many other diatomic molecules, although there may be exceptions, possibly including OH. Therefore one should consider each molecule and transition separately.

Bray and Hochstrasser (6) evaluated the rotational line intensity factors by explicitly summing the products of the TMEs in $K_1$ after neglecting the rotational contribution to the energy denominator, and using the appropriate one-photon
rotational line intensity factors. Instead of this laborious procedure, one can use
matrix notation to simplify the calculation. Such a method will be sketched here
for the two-photon case (7) and will also serve as an aid in understanding the
similar, but more complicated three photon calculation which follows.

Using the Born–Oppenheimer approximation and treating the rotational part of
the wavefunction as that of a symmetric top (11)

\[ \langle q v J \rangle = \langle \Phi(x_n) \rangle \langle \chi(R) \rangle \frac{(2J_1 + 1)^{1/2}}{8\pi} D_{m_1\Omega_1}^J(R). \]  

(7)

\[ D_{m_1\Omega_1}^J \] is the Wigner function, \( R \) the internuclear separation, and \( x_n \) the position of
the \( n \)th electron in molecular coordinates. \( m \) denotes the magnetic quantum
number and \( \Omega \) the projection of the total electronic angular momentum along
the internuclear axis. \( \Phi \) and \( \chi \) are the electronic and vibrational parts of the wave-
functions. If the exciting laser light is linearly polarized along the lab axis, the
product \( M \cdot E \) is (11)

\[ M \cdot E = e_0 E \sum_{n,p} r_n(-1)^p D_{\pm 1,p}^1(R) Y_{\pm 1}(\hat{z}). \]  

(8a)

For circularly polarized light

\[ M \cdot E = e_0 E \sum_{n,p} r_n(-1)^p D_{\pm 1,p}^1(R) Y_{\pm 1}(\hat{z}). \]  

(8b)

According to Eqs. (1), (7), and (8a) the transition rate \( K \) for linearly polarized
light is

\[ \hbar K = e_0^4 E^4 \sqrt{\sum_{a,b} \sum_{a,p} \sum_{a,q} \langle \Phi_a \rangle \langle \Phi_b \rangle \langle \chi_a \rangle \langle \chi_b \rangle} \]

\[ \times \sum_{J_l} \frac{(-1)^{p+q}}{(8\pi)^4} \frac{1}{\hbar(\omega_{a \Omega} - \omega)} (2J_l + 1) \frac{(2J_1 + 1)(2J_0 + 1)(2J_1 + 1)^{1/2}}{2} \]

\[ \times \langle D_{m_l\Omega_l}^J \rangle \langle D_{\pm 1,p}^1 \rangle \langle D_{m_1\Omega_1}^J \rangle \langle D_{m_1\Omega_1}^J \rangle \langle D_{m_1\Omega_1}^J \rangle \langle D_{m_1\Omega_1}^J \rangle \]  

(9)

If the small rotational contribution to the level energy is ignored and closure
is taken over the intermediate rotational states \( K \) becomes

\[ \hbar K = E^4 \sqrt{\sum_i \sum_{a,b} \sum_{p,q} \sum_{\chi_i} \langle \Phi_a \rangle \langle \chi_i \rangle \langle \chi_i \rangle} \]

\[ \times \frac{\mu_i^a \mu_i^b \mu_i^p \mu_i^q}{8\pi^2} \frac{1}{(8\pi)^4} \sum_{J_0} \frac{(2J_f + 1)^{1/2}}{\hbar(\omega_{a \Omega} - \omega)} (1100 | J0)(11pq | J\Delta\Omega) \]

\[ \times (J_f J - m0 | J_a - m)(J_f J - \Omega_a\Delta\Omega | J_f - \Omega_f)^2 \]  

(10)

\[ ^2 \text{After submission of this paper we learned that K. M. Chen and E. S. Yeung have published a paper} \]
\[ \text{entitled "Rovibronic Two-Photon Transitions of Symmetric Top Molecules." In this paper they} \]
\[ \text{calculate the two-photon rotational line strengths \( c \) using angular momentum theory. In addition they} \]
\[ \text{consider the case when the two photons have different polarizations and certain near resonant cases.} \]
\[ \text{The paper is to be found in Ref. (7).} \]
The notation for the Clebsch–Gordan coefficients is as given in Ref. (11) and the shorthand notation

\[ \mu_{\nu} = \mu_{\nu}^{(a)} = \langle \Phi_{\text{f}} | \sum_{a,\nu} r_{a,\nu} | \Phi_{\text{i}} \rangle, \]

\[ \mu_{\alpha'} = \mu_{\alpha'}^{(a)} = e_{\alpha} \langle \Phi_{\text{i}} | \sum_{b,\alpha} r_{b,\alpha} | \Phi_{\text{f}} \rangle \]

is used.

All selection rules for two-photon absorption can be derived from Eq. (10). The sum has three possible values of \( J \). Terms corresponding to \( J = 1 \) are identically zero, since the first Clebsch–Gordan coefficient vanishes. The \( J = 0 \) term is analogous to Rayleigh scattering, and has the selection rules

\[ p = -q, \quad m_f = m_g, \quad J_f = J_g, \quad p + q = \Delta \Omega = 0. \]

The dipole operator in this case belongs to the group of the irreducible tensor operators of order 0. This term appears only for transitions with \( \Delta \Omega = \Delta J = 0 \), i.e., \( Q \) branch two-photon transitions between states with the same value of \( \Omega \).

The terms with \( J = 2 \) have selection rules similar to those for Raman transitions, namely,

\[ \Delta J = 0, \pm 1, \pm 2, \quad m_f = m_g, \quad \Delta \Omega = p + q \]

and for

\[ \Delta \Omega = 0, \quad p = -q, \]

\[ \Delta \Omega = \pm 1, \quad p = \pm 1 - q, \]

\[ \Delta \Omega = \pm 2, \quad p = \pm 2 - q. \]

\( p \) and \( q \) are limited to the values \(-1\), \(0\), and \(1\). They represent the value of \( \Delta \Omega \) within the individual TMEs. The electronic part of the dipole operator belongs to the irreducible tensor operator of order 2. The vibrational part may be thought of as a weighted Franck-Condon factor. As seen in Eq. (6) if we ignore the vibrational contribution to the energy of the intermediate state, which is not totally unreasonable considering that the energy defect will usually be much greater than 10,000 cm\(^{-1}\), then the vibrational factor for two-photon excitation reduces to the same vibrational overlap integral as in single-photon absorption. For the cases considered here, where the final state is the lowest excited electronic state, the energy difference \( \hbar \omega_{q} - \omega \) will weight the product of overlap integrals toward the lower vibrational levels of the excited electronic intermediate states.

The rotational line strengths are obtained by squaring the expression in Eq. (10) and using the sum rule

\[ \sum_{m_1,m} (j_f j \mu_1 \mu_2 | jm)(j_f j \mu_1 \mu_2 | jm) = (2j_f + 1)(2j + 1) \delta_{j_1j_2} \delta_{m_1m_2}. \]

(11)

The rotational line strengths for the five cases \( \Delta \Omega = 0, \pm 1, \) and \( \pm 2 \) may then be written compactly as

\[ \Delta \Omega = \pm 2: \]

\[ \frac{S_{j_f j_\mu}}{(2j_f + 1)} = \frac{2}{15} (j_f 2 - \Omega_f \pm 2 j_\mu - \Omega_\mu) \mu_{+1} \mu_{+1}^{'} ; \]

\[ \Delta \Omega = \pm 1: \]

\[ \frac{S_{j_f j_\mu}}{(2j_f + 1)} = \frac{1}{15} (j_f 2 - \Omega_f \pm 1 j_\mu - \Omega_\mu) \mu_{+1} \mu_{+1}^{'} (\mu_{+1} \mu_{0}^{'} + \mu_{0} \mu_{+1}^{'} ) ; \]
\[ \Delta \Omega = 0: \]

\[
\frac{S_{j'j}}{(2j'+ 1)} = \frac{1}{9} \delta_{j j'} (\mu_0^2 + \mu_1 + \mu_{1'})^2
\]

\[ + \frac{1}{45} (j+2 - \Omega_0 | j_0 - \Omega_0| (2\mu_0 - \mu_{1'} - \mu_{1'})^2. (12) \]

where the electronic cofactors have been included, but not the vibrational. The vibrational part is the same for all cases.

The results are identical with those of Bray and Hochstrasser (6). A table of appropriate Clebsch-Gordan coefficients may be found in Condon and Shortley (12).

For circularly polarized light Eq. (8b) is used instead of Eq. (8a). The results obtained are almost the same as those shown in Eq. (12), except for a multiplicative factor of \( \frac{3}{2} \) and the fact that the Rayleigh term, \( J = 0 \), does not appear.

II.2. Two-Photon Rotational Line Intensity Factors for Intermediate Coupling

Both Bennett (13) and Kovacs (14) have calculated the one-photon rotational line intensities for electronic transitions between two doublet states with intermediate \((a)-(b)\) coupling. They start with the rotational line intensity factors for a state belonging to Hund's case \((a)\) and a complete set of wavefunctions for this state. Case \((b)\) and intermediate case wavefunctions are expressed as linear combinations of the basis wavefunctions for case \((a)\) through perturbation theory. Bennett's work is the more general, and his method will be followed in the calculation of the two-photon rotational line factors below. A detailed description of the perturbation calculation may be found in Ref. (15).

Bennett starts with the set of case \((a)\) states of energy

\[
E_{\alpha\Omega} = E_{\alpha\Omega}(R_e) + A(R_e)\Delta \Sigma - \gamma_v[S(S + 1) - \Sigma^2]
\]

\[ + B_v[J(J + 1) - \Omega^2 + S(S + 1) - \Sigma^2]
\]

\[ - D_v[J(J + 1) - \Omega^2 + S(S + 1) - \Sigma^2] (13) \]

where \( A(R_e) \) is the equilibrium multiplet splitting and \( \gamma_v(S(S + 1) - \Sigma^2) \) is the energy of the relativistic spin rotation interaction. The other terms have their usual spectroscopic meanings. The perturbation due to the interaction of the electron spin and the molecular rotation \( R \) is

\[
H^{12}_{12} = H^0_{21} = -2 \left( B_v - \frac{\gamma_v}{2} \right) (J_x S_x + J_y S_y) - \gamma_v \langle n\Omega | S \cdot N | n\Omega \rangle - \gamma_v [S^2 - S_z^2]. (14) \]

The intermediate state wavefunctions are then expressed as

\[
|\alpha\Omega M\rangle = \sum_{\Omega=\Lambda+\Sigma} \langle \alpha\Omega | \alpha\Omega \rangle |\alpha\Omega M\rangle (15) \]

where \( \alpha \) is the set of quantum numbers \( q, v, J \) and the transformation matrices for doublets are

\[
\langle \alpha, J + \frac{1}{2} | \alpha, \Lambda + \frac{1}{2} \rangle = \langle \alpha, J - \frac{1}{2} | \alpha, \Lambda - \frac{1}{2} \rangle = [\frac{1}{2}(1 + \Lambda Z U)]^{1/2},
\]

\[
\langle \alpha, J + \frac{1}{2} | \alpha, \Lambda - \frac{1}{2} \rangle = -\langle \alpha, J - \frac{1}{2} | \alpha, \Lambda + \frac{1}{2} \rangle = [\frac{1}{2}(1 - \Lambda Z U)]^{1/2}, (16) \]
where

\[ Z = Y - 2 + 4\tilde{D}_v \chi, \]
\[ X = (J + \frac{1}{2})^2 - \Lambda^2, \]
\[ U = 1/(2W), \quad Y = A/B_v, \]
\[ W = \frac{1}{2}[4(1 - 2\tilde{D}_v \chi - \frac{1}{2}\gamma_v)(J + \frac{1}{2})^2 + (Y - \tilde{\gamma}_v)(Y - 4 + 8\tilde{D}_v \chi + \tilde{\gamma}_v)\Lambda^2]^{1/2}, \]
\[ \tilde{D}_v = D_v/B_v, \quad \tilde{\gamma}_v = \gamma_v/B_v. \]

In the same manner as the single-photon absorption line strength is defined in Condon and Shortley (12) the two-photon line strength may be written as

\[ S(\alpha'\Omega', \alpha''\Omega'') = \sum_{M',M} \sum_{J,q} \left| \langle \alpha'\Omega' M' | Q^{(J)}_q | \alpha\Omega M \rangle \right|^2, \]  

(17)

where the sum over all electronic and vibrational states has been absorbed into the operator \( Q \). Using Eq. (12) we may write Eq. (17) as

\[ S(\alpha'\Omega', \alpha''\Omega'') = \sum_{J} \left( \langle \alpha'\Omega' | Q^{(J)}_q | \alpha''\Omega'' \rangle \right)^2 \mathcal{F}(\Omega', \Omega'') \delta(S', S'') \delta(\Sigma', \Sigma'') \]  

(18)

where

\[ S(\Lambda' + \Sigma'J', \Lambda'' + \Sigma''J'') = \frac{2J' + 1}{15} (J'2 - \Omega'\Delta\Omega \big| J' - \Omega'' \big)^2 \]
\[ \times (2\delta_{\Delta\Lambda, 2} + 1\delta_{\Delta\Lambda, 1} + \frac{1}{2}\delta_{\Delta\Lambda, 0}) + \frac{1}{2}\delta_{J', J} \delta_{\Delta\Lambda, 0} \text{ const.} \]  

(19)

is the rotational line factor.

The matrices \( \langle \alpha'\Omega' | Q^{(J)}_q | \alpha\Omega \rangle \) may in general have an arbitrary phase. In order to obtain the rotational line factors, independent of the electronic and vibrational parts of the line strengths for the intermediate \((a)-(b)\) coupling case it is necessary to assume a fixed phase relationship between \( \langle \alpha'\Lambda' - \frac{1}{2} | Q | \alpha\Lambda - \frac{1}{2} \rangle^2 \) and \( \langle \alpha'\Lambda' + \frac{1}{2} | Q | \alpha\Lambda + \frac{1}{2} \rangle^2 \). As is customary in the calculation of one-photon rotational line strengths we shall assume the squares of the two matrices to be equal. The integral over the internuclear separation depends only weakly on the spin orientation. This is shown by the fact that potential energy curves for the doublet components run parallel in most diatomic molecules. Under this assumption Eq. (18) may be rewritten as

\[ S(\alpha'\Omega', \alpha''\Omega'') = S_2(\alpha', \alpha'') \mathcal{F}(\Omega' J', \Omega'' J'') \delta(S', S'') \delta(\Sigma', \Sigma'') \]  

(20)

where \( S_2(\alpha', \alpha'') \) is the two-photon band strength.

Under these assumptions the intermediate case line strength in lowest order perturbation theory will be

\[ S(\alpha'N', \alpha''N'') \]
\[ = \sum_{M',M} \sum_{\gamma, J} \sum_{\Omega', \Omega''} \left( \langle \alpha'N' | \alpha'\Omega' \rangle \langle \alpha'\Omega' M' | Q^{(J)}_q | \alpha''\Omega'' M'' \rangle \langle \alpha''N'' | \alpha''\Omega'' \rangle \right)^2. \]  

(21)

Summing Eq. (21) over the magnetic quantum numbers \( M' \) and \( M \) and using the results of Eqs. (12), (18), (19), and (20) the line strength for two-photon transitions in doublet diatomic molecules belonging to the intermediate coupling case is

\[ S(\alpha'N', \alpha''N'') = \left[ \sum_{\Omega', \Omega''} \langle \alpha'N' | \alpha'\Omega' \rangle S(\alpha'\Omega', \alpha''\Omega'')^{1/2} \langle \alpha''N'' | \alpha''\Omega'' \rangle \right]^2 \]  

(22)
and the two-photon rotational line factor for the intermediate case is

$$\mathcal{J}(N'J', N''J'') = \left[ \sum_x \langle \alpha' N' | \alpha' \Lambda' + \Sigma' \rangle \mathcal{J}(\Lambda' + \Sigma' J', \Lambda'' + \Sigma'' J'')^{1/2} \langle \alpha'' N'' | \alpha'' \Lambda'' + \Sigma'' \rangle \right]^2.$$  

Equations (12), (16), and (23) were used to generate the tables of two-photon rotational line factors for the intermediate coupling case which may be found in the Appendix to this paper. There are separate tables for $\Delta \Lambda = 0, \pm 1, \text{and} \pm 2$.

Using Table VI in the Appendix we have calculated the two-photon rotational line intensity factors for the $(A^\Sigma^+ \leftrightarrow X^\Pi)$ transition of NO. The results are shown in Fig. 2. Here $\mathcal{J}_{J',J''}(2J'' + 1)$ is plotted against $J''$. $\mathcal{J}_{J',J''}$ is used as a shorthand notation for $\mathcal{J}(N'J', N''J'')$. It is apparent that the $Q_{12}$ and $Q_{22}$ branches have significant intensities only for very small values of $J''$, whereas the $Q_{11}$ and $Q_{12}$ branches are more than three orders of magnitude smaller than the other rotational branches of the $A-X$ bands of NO.

II.3. Three-Photon Absorption

The three-photon excitation rate $K$ may be obtained in a similar way to the two-photon rates (8).

$$\hbar K = \left| \sum_{i,h} \frac{\langle \psi_i | \mathbf{M} \cdot \mathbf{E} | \psi_h \rangle \langle \psi_i | \mathbf{M} \cdot \mathbf{E} | \psi_h \rangle \langle \psi_h | \mathbf{M} \cdot \mathbf{E} | \psi_g \rangle}{\hbar(\omega_{ih} - \omega)\hbar(\omega_{ih} - 2\omega)} \right|^2. \tag{24}$$

For the absorption of three-photons there are 19 possible combinations of virtual rotational, vibrational, and electronic transitions. Thus in analogy to Eq. (1), Eq. (24) would be separable into 19 sums. For homonuclear diatomics only one of these sums is different from zero:

$$\hbar K = \left| \sum_{i,h} \frac{\langle q_i \psi_i J_i | \mathbf{M} \cdot \mathbf{E} | q_i \psi_i J_i \rangle \langle q_i \psi_i J_i | \mathbf{M} \cdot \mathbf{E} | q_h \psi_h J_h \rangle \times \langle q_h \psi_h J_h | \mathbf{M} \cdot \mathbf{E} | q_g \psi_g J_g \rangle}{\hbar(\omega_{ih} - \omega)\hbar(\omega_{ih} - 2\omega)} \right|^2. \tag{25}$$

Therefore, the different contributions have to be analyzed separately for each molecule. This is more difficult than in the two-photon case.

The best method to calculate the different contributions to the rate constant $K$ would be the use of a theoretical model for the molecule under consideration. Such an evaluation would provide also the rotational line intensity factors. For the following calculations, we will restrict ourselves to an approximation valid in many cases: that Eq. (25) is the dominant term for the rate of excitation. This is valid for homonuclear diatomic molecules and may be a good approximation for many transitions in heteronuclear diatomic molecules. However, for heteronuclear diatomics, there are 18 other contributions to the rate of excitation, 6 of which have two electronic TMEs, and 12 of which have a single electronic TME. In principle any of these terms might be significant because of accidental resonances, etc. Thus each case must be examined separately.

It is important to recognize that the two- and three-photon rotational line factors are approximations. This is because the rotational energy contributions
Fig. 2. The dependence on the rotational quantum number $J'$ of the reduced two-photon rotational line intensity factors $S_{J''}(2J'' + 1)$ for the electronic transitions between two doublet states, which belong to the intermediate coupling case. The calculations were performed for the ($A^2\Sigma^+ \rightarrow X^2\Pi$) $\gamma$ bands of NO. (a) $O$ and $P$ branches; (b) $Q$ branches (one should notice the strong enhanced scale in the lower part) (c) $R$ and $S$ branches.
and several other small terms have been neglected in their calculation. If this were not done, one would be reduced to considering each molecule on the basis of its specific quantum mechanical representation.

Substitution of Eqs. (8a) and (7) into Eq. (25) yields the three-photon symmetric top excitation rate for linearly polarized light,

\[
\hbar K = E^6 \left| \sum_{i,h} \sum_{\mu,a,r} \mu_{\mu,a} \mu_{\mu,a} \sum_{x_i x_h} \langle \chi_i | x_i \rangle \langle \chi_i | x_h \rangle \langle \chi_h | x_h \rangle \right.
\]
\[
\times \sum_{J_i J_h} (-1)^{p+q+r} \frac{(2J_i + 1)(2J_h + 1)((2J_g + 1)(2J_f + 1))^{1/2}}{\hbar(\omega_{i0} - \omega)\hbar(\omega_{h0} - 2\omega)}
\]
\[
\times \langle D_{i0}^{J_i} D_{0i}^{J_i} D_{0h}^{J_h} \rangle \langle D_{i0}^{J_i} D_{0i}^{J_i} D_{0h}^{J_h} \rangle \langle D_{i0}^{J_h} D_{0h}^{J_h} D_{0i}^{J_i} \rangle \langle D_{i0}^{J_h} D_{0i}^{J_h} D_{0h}^{J_i} \rangle \right|^2. \tag{26}
\]

Again, we ignore the rotational contributions to the level energy denominators and take closure over the intermediate rotational states \(J_i\) and \(J_h\). The remaining integral may be evaluated by using the Wigner function sum rule. Thus the rate \(K\) can be written as

\[
\hbar K = E^6 \left| \sum_{i,h} \sum_{\mu,a,r} \mu_{\mu,a} \mu_{\mu,a} \sum_{x_i x_h} \langle \chi_i | x_i \rangle \langle \chi_i | x_h \rangle \langle \chi_h | x_h \rangle \right.
\]
\[
\times \frac{8\pi^2}{(8\pi)^6 \hbar(\omega_{i0} - \omega)\hbar(\omega_{h0} - 2\omega)} \left( \frac{2J_f + 1}{2J_g + 1} \right)^{1/2} \sum_{J=0}^{J+1} \sum_{J'=J-1}^{J+1} (1100|J0)
\]
\[
\times (11pq|Jp + q)(J100|J0)(J1p + qr|J'\Delta\Omega)
\]
\[
\times (JfJ' - \Omega_f\Delta\Omega|Jg - \Omega_g)(JfJ' - m0|Jg - m) \right|^2. \tag{27}
\]

Expanding the sums over \(J\) and \(J'\), only three terms are different from zero

\[
\hbar K = E^6 \left| \sum_{i,h} \sum_{\mu,a,r} \mu_{\mu,a} \mu_{\mu,a} \sum_{x_i x_h} \langle \chi_i | x_i \rangle \langle \chi_i | x_h \rangle \langle \chi_h | x_h \rangle \right.
\]
\[
\times \frac{8\pi^2}{(8\pi)^6 \hbar(\omega_{i0} - \omega)\hbar(\omega_{h0} - 2\omega)} \left( \frac{2J_f + 1}{2J_g + 1} \right)^{1/2}
\]
\[
\times \{(1100|00)(11pq|00)(0100|10)(010r|1\Delta\Omega)(JfJ1 - \Omega_f\Delta\Omega|Jg - \Omega_g)
\]
\[
\times (JfJ1 - m0|Jg - m) + (1100|20)(11pq|2p + q)(2100|10)
\]
\[
\times (21p + qr|1\Delta\Omega)(JfJ1 - \Omega_f\Delta\Omega|Jg - \Omega_g)(JfJ1 - m0|Jg - m)
\]
\[
+ (1100|20)(11pq|2p + q)(2100|30)(21p + qr|3\Delta\Omega)
\]
\[
\times (JfJ3 - \Omega_f\Delta\Omega|Jg - \Omega_g)(JfJ3 - m0|Jg - m) \right|^2. \tag{28}
\]

Again the rotational line strengths are calculated by taking the square of the expression in Eq. (28) and by using Eq. (11) for the evaluation of the sum of
Clebsch–Gordan coefficients. A table of the appropriate Clebsch–Gordan coefficients has been calculated by Falkhoff et al. (16). The three-photon rotational line strengths $S_{\Delta \Omega}$ are then given by

$$S_{\pm 3} = \frac{4}{175} (2J_f + 1)(J_f 3 - \Omega_f \pm 3 \mid J_o - \Omega_o)^2 (\mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2), \tag{29a}$$

$$S_{\pm 2} = \frac{2}{105} (2J_f + 1)(J_f 3 - \Omega_f \pm 2 \mid J_o - \Omega_o)^2$$

$$\times (\mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2 + \mu_{z_1} \mu_0 \mu_{z_1}''^2 + \mu_0 \mu_{z_1}' \mu_{z_1}''^2), \tag{29b}$$

$$S_{\pm 1} = \frac{1}{27} (2J_f + 1)(J_f 1 - \Omega_f \pm 1 \mid J_o - \Omega_o)^2 [\mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2 + \mu_{z_1} \mu_0 \mu_{z_1}''^2 + 6 \mu_{z_1} \mu_{z_1}''^2]$$

$$- \mu_0 \mu_0 \mu_0''^2 + \frac{1}{2} \{ \mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2 + \mu_{z_1} \mu_{z_1}''^2 + 6 \mu_{z_1} \mu_{z_1}''^2 \}$

$$+ 2 \mu_0 \mu_0 \mu_0''^2 + 3 \mu_0 \mu_0 \mu_0''^2 - 3 \mu_0 \mu_0 \mu_0''^2; \tag{29c}$$

$$S_0 = \frac{1}{27} (2J_f + 1)(J_f 0 - \Omega_0 0 \mid J_o - \Omega_o)^2 [\mu_0 \mu_0 \mu_0''^2 + \mu_{z_1} \mu_{z_1}''^2 - \mu_{z_1} \mu_{z_1}''^2]$$

$$+ \frac{1}{2} \{ \mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2 + 2 \mu_{z_1} \mu_{z_1}''^2 + 3 \mu_{z_1} \mu_{z_1}''^2 - 3 \mu_{z_1} \mu_{z_1}''^2 \}$$

$$- 3 \mu_0 \mu_0 \mu_0''^2 + 3 \mu_0 \mu_0 \mu_0''^2 + 4 \mu_0 \mu_0 \mu_0''^2]$$

$$+ \frac{1}{175} (2J_f + 1)(J_f 0 - \Omega_0 0 \mid J_o - \Omega_o)^2 [\mu_{z_1} \mu_{z_1}' \mu_{z_1}''^2 + \mu_{z_1} \mu_{z_1}''^2]$$

$$+ \mu_{z_1} \mu_{z_1}''^2 + \mu_{z_1} \mu_{z_1}''^2 + \mu_{z_1} \mu_{z_1}''^2 + \mu_{z_1} \mu_{z_1}''^2 + 2 \mu_0 \mu_0 \mu_0''^2. \tag{29d}$$

These results have been used to calculate the three-photon line intensity factors for a singlet $\Pi \leftrightarrow \Sigma$ transition where both states belong to Hund's case (a). An example of such a transition is the fourth-positive system of CO (A' $\Pi \leftarrow$ X' $\Sigma^+$). Since this is a $\Delta \Omega = +1$ transition Eq. (29c) is used for the calculation.

The line strengths for this case contain two terms, one with Clebsch–Gordan coefficients of the first order and one with coefficients of the third order. Both contributions are multiplied by different products of the electric dipole transition moments $\mu$. Because these moments are generally not known, it is not possible to calculate the total rotational line intensity factors. Therefore, we have calculated the rotational factors of first and third order separately.

The results are shown in Figs. 3a and b for the first and third order terms, respectively. These figures display the dependence of $\mathcal{S}_{\mu}(2J'' + 1)$ on the rotational quantum number $J''$ for the different rotational bands. The first order Clebsch–Gordan coefficient contributes only to the $P$, $Q$, and $R$ branches of the transition. The $J''$ dependence of $\mathcal{S}_{\mu}$ is the same as for a one-photon transition, except that the absolute value is different. And, of course, the transition dipoles
Fig. 3a. Three-photon reduced rotational line intensity factors $S_{J',J}/(2J'^* + 1)$ in dependence of $J''$ for Hund's case (a) states. Contributions of the first order Clebsch–Gordan coefficients. The calculations were performed for a ($\Pi \leftrightarrow \Sigma$) transition.

Fig. 3b. Three-photon rotational line intensity factors in dependence of $J''$ for the different rotational branches. Contribution of the third order Clebsch–Gordan coefficients, again calculated for ($\Pi \leftrightarrow \Sigma$) transitions. For $R(J'' = 0)$ is $S_{J',J} = 0$. 
Fig. 4. Two-photon rotational line intensity factors for CO and N₂ for the 0, Q, and S branches: ×××, CO(9,0); ○○○, CO(3,0); ▲▲▲, ++++, ●●●, N₂(5,0). Drawn line, theoretically expected $J$ dependence of $I_{J_p,J}(2J'' + 1)$. 
Fig. 5. Measured two-photon rotational line intensity factors for the $O_{11}$ branch of NO ($A^{3}Σ^{-}$, $v' = 0 ← X^{1}Π$, $v'' = 0$). × × ×, measured intensities. Full drawn line, theoretically expected $J''$ dependence of $S_{J''} =\frac{J''J}{(2J'' + 1)}$ for the intermediate coupling case (see Fig. 2a).

$μ$ are different, but they only act as scaling factors. The third order Clebsch–Gordan coefficient is nonzero for all seven rotational branches. The contribution to $ΔJ = ±1$ transitions are much smaller than to the other branches. It should be noted that the $ΔJ = ±2$ and $ΔJ = ±3$ transitions only have contributions from the third order element. Therefore, it should be possible to determine experimentally the ratio of the sum of products of transition dipole moments contained in the first and third order coefficients.

The results of Eq. (29) can be extended to the more general intermediate coupling scheme by calculations similar to those presented in Section II.2. For doublets the transformation matrices are given in Eqs. (15) and (16). For $ΔΩ = 0$, and ±1 there are two terms, and thus there would be an arbitrary constant in the line strength calculation. This could be resolved by comparison with the measured three-photon spectra.

If the one-photon contribution is dominant then the one-photon rotational line factors calculated by Bennett (13) will also apply to the three-photon case. For $ΔΩ = ±2$ or ±3 there is only a single element in the rotational line factors of order three, and thus there will be no arbitrary constant.

III. EXPERIMENTAL RESULTS

In this section we want to compare the calculated rotational line intensity factors with experimentally measured two- and three-photon spectra of different vibronic bands of electronic transitions in CO, N$_2$, and NO.

The integrated absorption cross section of a rotational line can be expressed by
Fig. 6. Doppler effect free registration of some rotational lines of the $\gamma(0)$ band of NO. The amplification and the scan rate is different for all five registrations. In the lower part the theoretically expected line intensities and positions are given. The drawn $Q_{11}$ and $Q_{21}$ line intensities are enhanced by a factor of 100.
TWO- AND THREE-PHOTON EXCITATION OF DIATOMICS

\[ \int \sigma(\nu) d\nu = \frac{\pi e^2}{mc^2} f(J',J'') \frac{N_{J'}}{N_{\text{tot}}}. \] (30)

\( N_{J'} \) is the population of the level \( J'' \) and \( N_{\text{tot}} \) is the total population. The oscillator strength \( f(J',J'') \) can be expressed by the band oscillator strength (I8)

\[ f(J',J'') = f(v',v'') \frac{1}{2J'' + 1} J_{J',J''} \] (31)

where \( J_{J',J''} \) is the rotational line intensity factor for a transition from \( J'' \) to \( J' \). The

FIG. 7. Measured three-photon rotational line intensity factors for the \((A^2 \Pi \leftrightarrow X^2 \Sigma^+)\) transition of CO. ×××, measured intensities. Line, theoretically expected \( J'' \) dependence, if only the first order elements are taken into account.
### TABLE III

**Two-photon Hön–London Factors for Doublet Transitions between States with Intermediate Coupling**

<table>
<thead>
<tr>
<th>$\Delta \lambda = \pm 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{011}$: $\frac{H_{-}(\pm \frac{1}{2})}{120J(J+1)(2J+1)} \left[ F_+ F_+ D^{(\frac{3}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 H_{-}(\mp \frac{1}{2},4) \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$P_{111}$: $\frac{H_{-}(\pm \frac{1}{2})}{60J(J+1)(3J-1)} \left[ F_+ F_+ D^{(\frac{1}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 D^{(\frac{1}{2},0)} D^{(-\frac{1}{2},2)} \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$Q_{111}$: $\frac{H_{+}(\pm \frac{1}{2})}{20J(J+1)(2J+1)(2J+3)} \left[ F_+ F_+ D^{(\frac{1}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 D^{(\frac{1}{2},0)} D^{(-\frac{1}{2},2)} \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$R_{111}$: $\frac{H_{+}(\pm \frac{1}{2})}{60J(J+1)(J+2)} \left[ F_+ F_+ D^{(\frac{3}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 D^{(\frac{3}{2},0)} D^{(-\frac{1}{2},2)} \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$S_{111}$: $\frac{H_{+}(\pm \frac{1}{2})}{120J(J+1)(2J+3)} \left[ F_+ F_+ D^{(\frac{1}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 D^{(\frac{1}{2},0)} D^{(-\frac{1}{2},2)} \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$N_{012}$: $\frac{H_{-}(\pm \frac{1}{2})}{120J(J+1)(2J-1)} \left[ F_+ F_+ D^{(\frac{1}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 H_{-}(\mp \frac{1}{2},4) \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$Q_{012}$: $\frac{H_{+}(\pm \frac{1}{2})}{60J(J+1)(J+1)} \left[ F_+ F_+ D^{(\frac{3}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 D^{(\frac{3}{2},0)} D^{(-\frac{1}{2},2)} \right]^{1/2} \right]$</td>
</tr>
<tr>
<td>$P_{012}$: $\frac{H_{+}(\pm \frac{1}{2})}{60J(J+1)(J+1)} \left[ F_+ F_+ D^{(\frac{3}{2},0)} + F_+ F_- D^{(-\frac{1}{2},2)} + 2 \left[ F_4 H_{+}(\mp \frac{1}{2},4) \right]^{1/2} \right]$</td>
</tr>
</tbody>
</table>

Relative population of a single rotational level $J''$ is given by

$$
\frac{N_{J''}}{N_{\text{tot}}} = \frac{1}{Q} (2J'' + 1) \exp \left\{ -\frac{hcE(J'',\nu'',\Sigma'')}{kT} \right\}
$$

(32)

where $E(J'',\nu'',\Sigma'')$ is the energy of the specific rotational level $J''$ in the vibrational state $\nu''$ of a state with the spin multiplicity $\Sigma''$. $Q$ is the partition function

$$
Q = \sum_{\Sigma''} \sum_{\nu''} \sum_{J''} (2J'' + 1) \exp \left\{ -\frac{hcE(J'',\nu'',\Sigma'')}{kT} \right\}.
$$

(33)
\[ \begin{array}{c}
\begin{align*}
\Delta \Lambda &= \pm 2 \\
R_{Q21} &= \frac{(2J+1)}{20J(3J+1)(2J-1)(2J+3)} \left[ F_R^+ F_+ D(\frac{3}{2},0) + F_R^+ F_- D(\frac{3}{2},2) - 2 \left[ F_4 D(\frac{3}{2},0) D(\frac{3}{2},2) \right]^{1/2} \right] \\
S_{Q21} &= \frac{H_{\frac{3}{2},A}}{60J(3J+1)(3J+2)} \left[ F_R^+ F_+ D(\frac{3}{2},0) + F_R^+ F_- D(\frac{3}{2},2) - 2 \left[ F_4 H_{\frac{3}{2},A} \right]^{1/2} \right] \\
T_{S21} &= \frac{(J-A+\frac{3}{2})}{120J(3J-1)(3J+3)} \left[ F_R^+ F_+ (J+A+\frac{3}{2}) + F_R^+ F_+ (J-A+\frac{3}{2}) + 2 \left[ F_4 H_{\frac{3}{2},A} \right] \right]^{1/2} \\
O_{22} &= \frac{(J-\frac{3}{2})}{120J(3J-1)(3J+1)} \left[ F_R^+ F_+ D(\frac{3}{2},0) + F_R^+ F_+ D(\frac{3}{2},2) + 2 \left[ F_4 D(\frac{3}{2},0) D(\frac{3}{2},2) \right]^{1/2} \right] \\
P_{22} &= \frac{(2J+1)}{20J(3J+1)(2J-1)(2J+3)} \left[ F_R^+ F_+ D(\frac{3}{2},0) + F_R^+ F_+ D(\frac{3}{2},2) + 2 \left[ F_4 D(\frac{3}{2},0) D(\frac{3}{2},2) \right]^{1/2} \right] \\
Q_{22} &= \frac{H_{\frac{3}{2},A}}{60J(3J+1)(3J+2)} \left[ F_R^+ F_+ D(\frac{3}{2},0) + F_R^+ F_+ D(\frac{3}{2},2) + 2 \left[ F_4 H_{\frac{3}{2},A} \right] \right]^{1/2} \\
R_{22} &= \frac{(J+A+\frac{3}{2})}{120J(3J+1)(3J+3)} \left[ F_R^+ F_+ (J+A+\frac{3}{2}) + F_R^+ F_+ (J-A+\frac{3}{2}) + 2 \left[ F_4 H_{\frac{3}{2},A} \right] \right]^{1/2} \\
S_{22} &= \frac{(J-A+\frac{3}{2})}{120J(3J+1)(3J+3)} \left[ F_R^+ F_+ (J+A+\frac{3}{2}) + F_R^+ F_+ (J-A+\frac{3}{2}) + 2 \left[ F_4 H_{\frac{3}{2},A} \right] \right]^{1/2} \\
\end{align*}
\end{array} \]

The measured rotational line intensity is therefore given by

\[ I = \text{const} \frac{J_{P',P}}{2J'' + 1} \frac{N_{P'}}{N_{\text{tot}}} \]  

(34)

III.1. Two-Photon Excitation of CO, N\textsubscript{2}, and NO

CO and N\textsubscript{2}. Single rotational lines in the fourth-positive system (\(A^1\Pi \leftrightarrow X^1\Sigma^+)\) of CO and in the Lyman–Birge–Hopfield system (\(a'\Pi_g \leftrightarrow X^1\Sigma^+\)) of N\textsubscript{2} are excited with a powerful narrow band frequency doubled tunable dye laser. The details of this experiment have been described earlier (Filseth \textit{et al.} (5)).

For a comparison of the measured line intensities with the calculated line intensity factor the measured intensities are divided by the relative level population (\(N_{\nu,J}/N_{\text{tot}}\)) and then adjusted to agree with the calculations at one value of \(J\). Because N\textsubscript{2} is a homonuclear diatomic molecule with nonzero nuclear spin of the \(^{14}\text{N}\) atoms (\(I = 1\)), an additional factor of degeneracy has to be taken into account in the determination of the level population. This factor is different for symmetric and antisymmetric rotational states. In the case of \(^{14}\text{N}_2\) the nuclear spin causes an odd–even staggering of the population in the ratio 2:1. This is observed clearly in the experiment (see Filseth \textit{et al.} (5)).

In the experiment the excitation of the (3,0) and (9,0) vibrational transitions of the fourth-positive system of CO and the (5,0) transition of the Lyman–Birge–
TABLE IV

Two-photon Hön–London Factors for Doublet Transitions between States with Intermediate Coupling

<table>
<thead>
<tr>
<th>( \Delta \hbar = +1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0_{11} : ( \frac{H_{-1,1}}{60(J-1)(2J-1)} )</td>
</tr>
<tr>
<td>[ f' F_+ (0, -\frac{1}{2}) + f'<em>- F</em>- (1, -\frac{1}{2}) + 2 f_4 (0, -\frac{1}{2}) (2, -\frac{1}{2}) ]</td>
</tr>
<tr>
<td>0_{11} : ( \frac{(J-1)^2}{120(J+1)(J-1)} )</td>
</tr>
<tr>
<td>[ f'<em>+ F</em>+ (1, -\frac{1}{2}) B_4 (0, 0) + f'<em>- F</em>- (1, -\frac{1}{2}) B_4 (2, 0) + 2 B_4 (1, 1) f_4 (\frac{1}{2}, \frac{1}{2}) ]</td>
</tr>
<tr>
<td>0_{11} : ( \frac{(2J+1)}{60(J-1)(2J+1)} )</td>
</tr>
<tr>
<td>[ f'<em>+ F</em>+ (0, 1, -\frac{1}{2}) B_4 (1, 0) + f'<em>- F</em>- (0, 1, -\frac{1}{2}) B_4 (1, 0) + 2 B_4 (0, 1) f_4 (\frac{1}{2}, \frac{1}{2}) ]</td>
</tr>
</tbody>
</table>

Hopfield system of \( N_2 \) have been recorded. The \( \alpha' \Pi_o - \chi' \Sigma'_o \) transition of nitrogen is an allowed transition for two-photon electric dipole and for one-photon magnetic dipole and electric quadrupole (19) excitation, but forbidden for one-photon electric dipole decay. Figure 4 shows the dependence of \( \mathcal{F}_{\mu \nu} / (2J'' + 1) \)
on the rotational quantum number $J''$ for the $O$, $Q$, and $S$ branches of these transition's rotational part only. The drawn line represents the expected value calculated by the rotational factors given in Eq. (12). The measured line intensities were normalized to the $S(0)$ lines of CO and N$_2$. The experimental values are an average of several recorded spectra. As displayed in Fig. 4, the variation of the theoretical and experimental line intensities with $J''$ are in good agreement. This is valid also for the $P$ and $R$ branch, and for the relative intensities of the different rotational branches. The observed deviations are believed to be caused mainly by variations of the laser power and by changes of the laser beam diameter. Both parameters contribute to the line intensities quadratically.

**NO.** With the same laser system we have excited NO in the $(A^2Σ^+ ← X^2Π)$ $γ$ bands. The $X^2Π$ ground state of NO belongs to a coupling case intermediate between Hund’s cases (a) and (b), whereas the upper state of the $γ$ bands belongs to Hund’s case (b). Therefore the measured line intensities have to be compared with those calculated for intermediate coupling. Due to the relativistic electron spin nuclear rotation interaction, all rotational levels of the upper state split into narrow doublets with the same $N$ but different $J$. This splitting is, up to $N' = 40$, smaller than the Doppler width of NO. Therefore, the two rotational branches, which originate from the same $J''$ level, but correspond to different $ΔJ$ transitions (e.g., $R_{21}(J'')$ and $S_{11}(J'')$), cannot be resolved with conventional spectroscopic methods. This is true for 20 of the 24 rotational branches. Only the $S_{21}$, $S_{22}$, $O_{12}$, and $O_{11}$ branch lines, which are $ΔJ = ±2$ transitions, consist of a single transition. In these bands we have therefore measured systematically the dependence of $F_{\mu r, \mu r}$ ($2J'' + 1$) on the rotational quantum number. This dependence is illustrated in Fig. 5 for the two-photon rotational line intensity factors of the $O_{11}$ branch of the $γ(0,0)$ band. In the experiment the intensities of lines with $J''$ up to 25½ were measured. The line in the figure connects rotational line intensity factors calculated from the equations from Table VI and displayed in Fig. 2. The agreement between the calculated and the measured two-photon rotational line intensity factors seems to be satisfactory.

To test the theoretical results for other rotational bands of NO, the correspond-
Two-photon Hönl–London Factors for Doublet Transitions between States with Intermediate Coupling

\[ \chi_{+1} \cdot \chi_{+1} = \left( \frac{\alpha}{\beta} \right) \Delta \frac{1}{2} \left( \frac{1}{2} \right) \]

<table>
<thead>
<tr>
<th>Term</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>0_{11}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{circ}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{1in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{2in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{3in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{circ 1in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{circ 2in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
<tr>
<td>0_{11}^\text{circ 3in}</td>
<td>\frac{1}{120(331)(221)(121)} \left[ r_{1}^2 f_{2} \left( \frac{1}{2} \right)^2 \right]</td>
</tr>
</tbody>
</table>

...ing transitions have to be recorded with a laser of narrow bandwidth and Doppler effect free excitation techniques. For a Doppler effect free registration of the rotational lines, the bandwidth of the exciting laser light was reduced to less than 140 MHz. The laser beam was collimated to a small parallel beam with a diameter of about 1.5 mm and reflected back into the fluorescence cell with a plane mirror. The experimental details are the same as those used in an experiment for simul-
TWO- AND THREE-PHOTON EXCITATION OF DIATOMICS

TABLE V—Continued

<table>
<thead>
<tr>
<th>( \Delta \Delta ):</th>
<th>( Q )</th>
</tr>
</thead>
</table>
| 521 : \[
\frac{1}{60(3+1)(2+1)} \left[ r' r_1, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, -\frac{1}{2}) + r'_1 r, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (2, -\frac{1}{2}) 0(2, \frac{1}{2}) \right] \right]^{1/2}
\]
| 521 : \[
\frac{1}{120(3+1)(2+1)} \left[ r'_1 r_1, (\frac{3}{2} + \frac{1}{2})^2 \ 0(2, -\frac{1}{2}) + r'_1 r, (\frac{3}{2} + \frac{1}{2})^2 \ 0(2, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (2, -\frac{1}{2}) 0(2, \frac{1}{2}) \right] \right]^{1/2}
\]
| 522 : \[
\frac{1}{120(3+1)(2+1)} \left[ r'_1 r_1, (\frac{1}{2} - \frac{1}{2})^2 \ 0(-1, -\frac{1}{2}) + r'_1 r, (\frac{1}{2} - \frac{1}{2})^2 \ 0(-1, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (0, -\frac{1}{2}) 0(0, \frac{1}{2}) \right] \right]^{1/2}
\]
| 522 : \[
\frac{1}{60(3+1)(2+1)} \left[ r'_1 r_1, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, -\frac{1}{2}) + r'_1 r, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (2, -\frac{1}{2}) 0(2, \frac{1}{2}) \right] \right]^{1/2}
\]
| \( c^\text{circ} \) \[
\frac{1}{32+1} \left[ r'_1 r_1, (\frac{3}{2} + \frac{1}{2})^2 \ 0(2, -\frac{1}{2}) + r'_1 r, (\frac{3}{2} + \frac{1}{2})^2 \ 0(2, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (2, -\frac{1}{2}) 0(2, \frac{1}{2}) \right] \right]^{1/2}
\]
| \( 522 \) : \[
\frac{1}{60(3+1)(2+1)} \left[ r'_1 r_1, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, -\frac{1}{2}) + r'_1 r, (\frac{3}{2} - \frac{1}{2})^2 \ 0(1, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (2, -\frac{1}{2}) 0(2, \frac{1}{2}) \right] \right]^{1/2}
\]
| \( 522 \) : \[
\frac{1}{120(3+1)(2+1)} \left[ r'_1 r_1, (\frac{1}{2} - \frac{1}{2})^2 \ 0(-1, -\frac{1}{2}) + r'_1 r, (\frac{1}{2} - \frac{1}{2})^2 \ 0(-1, \frac{1}{2}) - (2 \gamma^2 \gamma) \left[ r_1 (0, -\frac{1}{2}) 0(0, \frac{1}{2}) \right] \right]^{1/2}
\]

Doppler-free excitations were recorded for several lines of the \((O_{21} + P_{11}), (P_{21} + Q_{11}), (Q_{21} + R_{11}), (R_{21} + S_{11}), (Q_{20} + R_{10}), \) and \((R_{32} + S_{32})\) branches in the \(\gamma(0,0)\) transition. Some of these registrations are shown in the upper part of Fig. 6. It should be mentioned that the amplification and the scan speed is different in all five registrations. In the lower part of Fig. 6, the calculated line positions and relative line intensities are shown, including the lower state population. The intensity ratios of the \(P_{11}/O_{21}, S_{11}/R_{21}, \) and \(S_{12}/R_{22}\) lines agree well with the calculated values. As it is expected from the theory the \(Q\) lines do not appear. They should be a factor of 500 to 1000 lower than the corresponding \(P\) or \(R\) lines. This result can be seen also from Fig. 2. The relative line positions were calculated using a spin-splitting constant of \(\gamma = -86\) MHz (Wallenstein and Zacharias (3)).

The results shown in Figs. 5 and 6 indicate that the calculated and measured rotational line intensities are in good agreement for transitions which belong to the intermediate coupling case. Therefore, the expressions given in the preceding chapter for the calculation of the rotational line intensities provide reliable results for two-photon excitation of the majority of electronic transitions in diatomic molecules.

### III.2. Three-Photon Excitation of CO

According to the theory presented in Section II there should be first order and third order contributions to the rotational line intensities in three-photon excitation of diatomic molecules. It is very difficult to estimate the relative strength of the
Two-photon HönI–London Factors for Doublet Transitions between States with Intermediate Coupling

<table>
<thead>
<tr>
<th>Branch</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>P01</td>
<td>$\frac{H_{12}(J+1)}{60(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
<tr>
<td>P11</td>
<td>$\frac{(J+1) H_{12}}{120(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
<tr>
<td>P21</td>
<td>$\frac{H_{12}(J+1)}{60(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
<tr>
<td>P31</td>
<td>$\frac{(J+1) H_{12}}{120(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
<tr>
<td>P41</td>
<td>$\frac{H_{12}(J+1)}{60(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
<tr>
<td>P51</td>
<td>$\frac{(J+1) H_{12}}{120(J+1)(J+2)(J+3)} \left[ F_{2} F_{2} \frac{D(0,0)}{D(1,1)} + F_{2} F_{0} \frac{D(2,0)}{D(1,1)} + \frac{1}{2} \left[ \gamma_{4} \frac{D(0,0)}{D(1,1)} \right] \right]^{1/2}$</td>
</tr>
</tbody>
</table>

Two accompanying electronic transition dipole moments. However, these dipole moments are the same for all rotational branches in the first and third order, respectively. The third order J-dependent prefactors can be seen in Figs. 3a and 3b to be 10 to 100 times smaller than the first order contributions. Further, the first order term contributes only to the $P$, $Q$, and $R$ branches, whereas the third order contributes to all seven possible branches.
Table VI—Continued

\[ \Delta^2 F \]

<table>
<thead>
<tr>
<th>( Q_{22} )</th>
<th>[ \frac{\hbar^2 (J+1)}{60(J+1)(2J+1)} \left{ F_+ F_- D(0, \frac{3}{2}) + F_+ F_+ D(0, \frac{1}{2}) + 2 \left[ F_+ D(-1, -\frac{1}{2}) D(0, \frac{3}{2}) \right] \right}^{1/2} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{22} )</td>
<td>[ \frac{J+1}{120(J+1)(2J+1)} \left{ F_+ F_- D(J+1, -\frac{1}{2}) + F_+ F_+ D(J+1, \frac{3}{2}) + 2 B_+ D(J+1, \frac{1}{2}) \left[ F_+ B_+ D(J+1, -\frac{1}{2}) \right] \right}^{1/2} ]</td>
</tr>
<tr>
<td>( S_{22} )</td>
<td>[ \frac{J+1}{60(J+1)(2J+1)} \left{ F_+ F_- D(-J, -\frac{1}{2}) + F_+ F_+ D(-J, \frac{3}{2}) + 2 \left[ F_+ D(J, -\frac{1}{2}) D(J+1, \frac{1}{2}) \right] \right}^{1/2} ]</td>
</tr>
</tbody>
</table>

Both in the experiments described here and in Faisal, et al. (4), where the three-photon excitation spectra of the fourth-positive system of CO was measured, no lines belonging to the \( T \) and \( IV \) branches \((\Delta J = \pm 3)\) and, with a single exception, no rotational lines of the \( S \) and \( O \) branches \((\Delta J = \pm 2)\), were observed. Therefore it is only possible to set a lower limit on the ratio of the accompanying sums of products of transition dipole moments. Referring to Figs. 3a and 3b the ratio of the rotational line factor terms of first order to the terms of third order where \( \Delta J > k \) \((i.e., \text{the } N, O, S, \text{and } T \text{ branches of the third order contribution})\) is roughly 10:1. The experimental sensitivity is high enough that lines which were 10 to 100 times less intense than the \( P, Q, \text{and } R \) branch lines actually measured would have been seen. Therefore the variation of rotational line intensities was analyzed by neglecting the third order contribution to the measured \( P, Q, \text{and } R \) branch lines. Figure 7 displays the dependence of the reduced three-photon rotational line intensity factors \( F_{\mu \nu \lambda} / (2J'' + 1) \), on the rotational quantum number \( J'' \). Again the measured line intensities have been divided by the relative rotational state population. The curves in Fig. 7 give the theoretical dependence of the rotational line intensity factors on rotational quantum number, when only the first order contributions from Eq. (29) are taken into account. The fluctuations are somewhat larger than in the corresponding curves for two-photon excitation. This is not surprising because fluctuations in laser power and beam profile contribute to the line intensities by the third power. Nevertheless the agreement between the theory of Section II and the measurements is quite satisfactory.

IV. SUMMARY

The basic theory for calculating rotational line intensities in two-photon and three-photon excitation of diatomic molecules is presented. A conceptual framework is used that allows the theory to be easily generalized to \( N \)-photon excitation. The existing theory for two-photon excitation between two Hund’s case (a) states (6, 7) is extended to Hund’s case (b) and the intermediate (a)-(b) coupling schemes following the work of Bennett (13) on one-photon rotational line factors.
TABLE VII

Two-photon Hönl–London Factors for Doublet Transitions between States with Intermediate Coupling

<table>
<thead>
<tr>
<th>( \Delta \Lambda = -2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O^1_{11} = \frac{(J^+ - \frac{5}{2})}{120(J - 1)(2J - 1)} )</td>
</tr>
<tr>
<td>[ F^+_J F^- (J^+ + \frac{1}{2}) + F^-_J F^+ (J^+ + \frac{1}{2}) + 2 \left[ F^+_J H (J^+ + \frac{1}{2}) \right]^{1/2} ]</td>
</tr>
<tr>
<td>( P^1_{11} = \frac{H^+_J}{60(J + 1)(J - 1)} )</td>
</tr>
<tr>
<td>[ F^+_J F^+ (J^+ - \frac{1}{2}) + F^-_J F^- (J^+ - \frac{1}{2}) + 2 \left[ F^+_J H (J^+ - \frac{1}{2}) \right]^{1/2} ]</td>
</tr>
<tr>
<td>( Q^1_{11} = \frac{(2J + 1)}{20(J + 1)(2J - 1)(2J + 3)} )</td>
</tr>
<tr>
<td>[ F^+_J F^+ (J^+ + \frac{1}{2}) + F^-_J F^- (J^+ - \frac{1}{2}) + 2 \left[ F^+_J H (J^+ + \frac{1}{2}) \right]^{1/2} ]</td>
</tr>
<tr>
<td>( R^1_{11} = \frac{H^+_J (2J + 1)}{120(J + 1)(2J + 3)} )</td>
</tr>
<tr>
<td>[ F^+_J F^+ (J^+ + \frac{1}{2}) + F^-_J F^- (J^+ - \frac{1}{2}) + 2 \left[ F^+_J H (J^+ + \frac{1}{2}) \right]^{1/2} ]</td>
</tr>
<tr>
<td>( S^1_{11} = \frac{(J^+ - \frac{5}{2})}{120(J - 1)(2J - 1)} )</td>
</tr>
<tr>
<td>[ F^+_J F^- (J^+ + \frac{1}{2}) + F^-_J F^+ (J^+ - \frac{1}{2}) + 2 \left[ F^+_J H (J^+ - \frac{1}{2}) \right]^{1/2} ]</td>
</tr>
</tbody>
</table>

for the intermediate case. Algebraic expressions for the rotational line intensity factors for two-photon transitions between doublet states with \( \Delta \Lambda = 0, \pm 1, \) and \( \pm 2 \) are tabulated. These tables are to be found in the Appendix. The method of calculating the intermediate case three-photon rotational line factors is sketched.

Careful examination of the intermediate states involved in two- and three-photon excitation shows that for the molecules studied here, for all homonuclear diatomics, and probably for most other diatomics, the most important contributions
### Table VII—Continued

<table>
<thead>
<tr>
<th>( \Delta \Lambda = -2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{Q21} ): ( \frac{(2z+1)}{200(3z+1)(2z-1)(2z+3)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
<tr>
<td>( S_{R21} ): ( \frac{H_{-}(2,4)}{600(3z+1)(4z+2)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
<tr>
<td>( T_{S21} ): ( \frac{(3z+1)}{120(4z+1)(4z+2)(4z+3)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
<tr>
<td>( O_{20} ): ( \frac{H_{+}(1,4)}{600(4z+1)(4z+2)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
<tr>
<td>( P_{22} ): ( \frac{(2z+1)}{200(4z+1)(4z+2)(4z+3)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
<tr>
<td>( Q_{22} ): ( \frac{H_{-}(2,4)}{600(4z+1)(4z+2)} ) { ( F^* ) ( D(\frac{1}{2},0) ) ( F ) ( D(\frac{1}{2},0) ) } { ( F ) ( D(\frac{1}{2},0) ) } }^{1/2}</td>
</tr>
</tbody>
</table>

To the excitation rate will come from intermediate states belonging to electronic states other than the initial and final state.

Finally, an experimental verification of the theory is given for the two-photon excitation of CO, N\(_2\), and NO and the three-photon excitation of CO.

**APPENDIX**

Using Eqs. (12) and (17) and the elements of the transformation matrix (Eqs. (16)) we have derived explicit expressions for two-photon excitation between doublet states which belong to a coupling intermediate between Hund's cases (a) and (b). These expressions are given in the following tables without the accompanying electronic transition dipoles, except the \( Q \) branches in \( \Delta \Lambda = 0 \) transitions. For brevity of presentation and convenience of computation we used the abbreviations:

\[
D(X, Y) = (J + X)^2 - (\Lambda + Y)^2.
\]

\[
H_{\pm}(X, Y) = (J \pm \Lambda + X)^2 - Y.
\]

\[
B_{\pm}(X, Y) = (J \pm 2\Lambda + X)^2 - Y.
\]

\[
G_{\pm} = J(J + 1) - 3(\Lambda \pm \frac{1}{2})^2.
\]

\[
F_{\pm} = 1 \pm AZU.
\]

\[
F_4 = F_+ F_- F_+ F_- = (1 - \Lambda^2 Z^2 U^2)(1 - \Lambda^2 Z^2 U^2).
\]
The primed quantities refer to the upper and the unprimed to the lower state of the electronic transition. In Tables III, IV, V, VI, VII the Hoenl–London factors are given for $\Delta \Delta = +2, +1, 0, -1, -2$ transitions, respectively.

ACKNOWLEDGMENT

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