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A (3+1) resonance enhanced multiphoton ionization study of the $C^1\Sigma^+$ and $E^1\Pi$ states of CO: Polarization dependence used to probe electronic excitation routes and electronic character

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The three-photon excitations of the $C^1\Sigma^+$ and $E^1\Pi$ states have been investigated with resonance enhanced multiphoton ionization spectroscopy as a function of the polarization of the excitation light. From the observed polarization dependence the contributions of the various excitation routes have been determined, and the electronic character of these states has been analyzed. The results indicate that the $v'=0$ and 1 vibrational levels of the $E^1\Pi$ state have slightly different electronic characters.

I. INTRODUCTION

The electronic excited states of CO have since long been the subject of extensive experimental and theoretical research. By vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) absorption and emission techniques electronic states have been observed up until excitation energies close to the lowest ionization energy. The application of multiphoton excitation techniques to study the excited states of CO is of more recent date. Examples are found in the studies of the $A^1\Pi$, $B^1\Sigma^+$, and $R^1\Pi$ states.

One of the attractive features of multiphoton excitation is found in the selection rules on $\Delta\Lambda$ and $\Delta J$, which enable a larger range of transitions to be studied than the regular one-photon transitions. Another fundamental difference between one- and multiphoton absorption arises from the dependence of the signal strength on the polarization of the excitation light. One-photon transitions are independent of this polarization, but multiphoton transition intensities do show a polarization dependency, a characteristic often used to determine the symmetry of electronic transitions. An $n$-photon transition from state $|g\rangle$ to state $|f\rangle$ can be regarded as proceeding along an excitation route consisting of $n$ consecutive one-photon transitions via $(n-1)$ virtual intermediate states $|i\rangle$. In each of these one-photon transitions $\Lambda$ may change by 0 or $\pm 1$, depending on whether the transition takes place via the $z$-component of the transition dipole moment in the molecule fixed frame (parallel transition) or via the $(x\pm iy)$-component (perpendicular transition). An excitation route in an $n$-photon transition may thus be characterized by the number of parallel and the number of perpendicular transitions that occur. For $n$-photon transitions in which $\Delta\Lambda$ is larger than $(n-2)$ this excitation route can be identified unambiguously since for such transitions $\Delta\Lambda$ requires at least $(n-1)$ perpendicular transitions. However, transitions in which $\Delta\Lambda$ is smaller than or equal to $(n-2)$, are in principle possible via more than one excitation route. Since these various routes each show a unique dependence on the polarization, the polarization behavior of an electronic transition can show whether one particular excitation route dominates the transition, or whether several excitation routes interfere. It is evident that the dominance of one or more routes is intimately connected with the symmetries of the virtual states involved in the excitation process and the electronic character of the excited state under investigation. The polarization behavior can thus serve as a probe for the electronic character and possible perturbations of an excited state.

Beautiful examples of the use of the polarization dependence of a multiphoton transition to determine the dominant excitation route are observed in the three-photon excitation studies of the $B$ and $C'$ systems of NH$_3$. Here, the dominance of one particular excitation route could nicely be demonstrated by the comparison of the experimental polarization behavior and the theoretically predicted behavior for each of the possible routes. For most of the multiphoton transitions studied in several species, however, such a clear dominance is not observed. Although this indicates that usually more than one excitation route contributes to the signal strength, relative contributions of the various routes have as yet not been determined. For the specific case of CO, examples in which more than one route appears to be involved, are found in the two-photon excitation studies of the $B^1\Sigma^+$ state and the three-photon excitation studies of the $A^1\Pi$ state.

In the present study we will be concerned with the three-photon transitions from the ground state of CO to the $C^1\Sigma^+$ and $E^1\Pi$ states as investigated with resonance enhanced multiphoton ionization (REMPI) spectroscopy. The transition to the $C^1\Sigma^+$ state as well as the transition to the $E^1\Pi$ state has in principle contributions from two excitation routes since for both transitions $\Delta\Lambda<(n-2)$. We have determined to which extent each excitation route contributes to the transition by a study of the polarization dependence of the strength of the various rotational transitions. In general, the rotational selection rules for a three-photon transition allow $\Delta J=0,\pm 1,\pm 2$, and $\pm 3$ transitions. In the case of identical photons it can be shown that the $\Delta J=0,\pm 1$ transitions derive their transition probability from the first and third rank components of the hyperpolarizability tensor, while the $\Delta J=\pm 2,\pm 3$ transitions...
tions are only possible via the third rank component. The
means to characterize a transition in terms of excitation
routes derives from the fact that each excitation route has
a unique ratio of the contributions of first and third rank
components. These contributions can be determined sepa-
rately by a study with polarized excitation light: with lin-
early polarized light both components contribute, but with
circularly polarized light the transition probability arises
only from the third rank component.

The results of our study of the $C^1\Sigma^+$ and $E^1\Pi$ states
with linearly and circularly polarized excitation light re-
veal that the three-photon transitions to these states cannot
be described adequately by a single excitation route; both
possible excitation routes need to be taken into account
explicitly. It will be shown that due to the interference
between both excitation routes the $\Delta J=0, \pm 1$ transitions
dominate the excitation spectra completely. Only by using
circularly polarized light, with which the contribution of
the first rank component vanishes, can $\Delta J=\pm 2$ and $\pm 3$
transitions be observed for the first time. This observation
will be demonstrated to enable a determination of the rel-
ative contributions of the various excitation routes to the
total transition probability. The polarization dependence
of the excitation spectra consequently allows for an inter-
pretation in terms of the possible excitation routes. Apart
from such an interpretation at a molecular level, it will be
shown that the predominant atomic character of the mo-
lecular orbitals under consideration can elucidate the ex-
perimental results at an atomic level. Finally, the differ-
ences between the polarization behaviors of different
vibrational levels in the excited state will be discussed. In
contrast to the $C^1\Sigma^+$ state, where the $\nu'=0$ and 1 levels
exhibit a similar polarization dependence, these vibrational
levels show a markedly different behavior in the $E^1\Pi$ state.
The origin of this difference is believed to arise from
slightly different electronic characters associated with the
two vibrational levels.

II. EXPERIMENT

In our experiments a molecular beam, produced by a
free jet expansion of either 3 atm pure CO or 5% CO in
He, was intersected at right angles by the focused beam of
the excitation laser. Ions generated at the intersection point
were focused by homebuilt ion optics into the entrance
aperture of a quadrupole mass filter, which was oriented
collinearly with the expansion direction of the molecular
beam. A schematic diagram of this setup is depicted in
Fig. 1.

The optical excitation was provided by the frequency-
doubled output of a dye laser (Lumonics HyperDye 300)
operating on DCM, which was pumped by an excimer
laser (Lambda Physik EMG103 MSC) operating on XeCl
(308 nm). Frequency doubling of the fundamental laser
light was accomplished by an Inrad Autotracker II unit.
For some experiments we used the fundamental wave-
length of a dye laser operating on Coumarin 440. The lin-
early polarized light (purity 1000:1) with a temporal width
of 8 ns and an energy width of 0.15 cm$^{-1}$ was directed into
a Pockels cell (Electro Optic Developments PC105).

Changing the voltage on a KD*P crystal incorporated into
this cell enabled the continuous modification of the polar-
ization of the excitation light. Circularly polarized light
with a purity of 300:1 could be obtained in this way. The
excitation light was focused into the excitation region by a
lens with a focal length of 10 cm. The maximum averaged
power density in the focus of $\sim 50 \mu m$ was in the order of
$10^{10}$ W/cm$^2$.

The pulsed supersonic expansion was generated by a
pulsed valve (General Valve Iota One system) with a noz-
kle diameter of 100 $\mu m$. Molecular beam pulses with a
duration of 300 $\mu s$ were generated at a frequency of 15 Hz.
The expansion occurred into a differentially pumped vac-
uum system consisting of two chambers. In the main
chamber excitation and ionization were performed at a dis-
tance of 3 mm (30 nozzle diameters) from the nozzle. The
second chamber, separated from the main chamber by a
beam skimmer with a diameter of 2 mm, contained the
quadrupole mass filter (UTI 100C), which was set at the
mass of CO (27 amu). The ions were detected with a 16
dynodes BeO multiplier.

The main chamber was pumped by a Leybold Heraeus
DI 3000 oil diffusion pump (3000 $\ell$/s) backed by a Ley-
bold Heraeus D40B rotary pump, while the quadrupole
chamber was pumped by a Leybold Heraeus Turbovac 220
turbomolecular pump (220 $\ell$/s) backed by a Leybold Her-
aeus D20A rotary pump. Under the common experimental
conditions of 3 atm backing pressure, the pressure in the
main chamber was $10^{-5}$ mbar and in the quadrupole
chamber $10^{-6}$ mbar. Expansion of pure CO under such
conditions led to a rotational temperature of $\sim 13$ K as
was deduced from the rotationally resolved excitation spectra.

The signal obtained from the BeO multiplier was am-
plicated by a preamplifier (Princeton Applied Research
211), whose output was connected to both a boxcar inte-
grator (Stanford Research 250) and an oscilloscope. The
output of the boxcar was digitized with a 14 bits A/D
converter and averaged in the computer. In a typical wave-
length scan steps of 0.05 or 0.1 cm$^{-1}$ were taken and the ion signal was integrated during 2–8 s.

III. RESULTS

In Fig. 2 the rotationally resolved (3+1) REMPI spectra of the $C^1\Sigma^+(v'=0) \rightarrow X^1\Sigma^+(v''=0)$ and the $C^1\Sigma^+(v'=1) \rightarrow X^1\Sigma^+(v''=0)$ transitions using linearly and circularly polarized light are depicted. In agreement with previous one-photon absorption studies$^2$ it is found that the transition to the $C^1\Sigma^+(v'=1)$ level is an order of magnitude less intense than the transition to the $C^1\Sigma^+(v'=0)$ level. The transition to the $v'=0$ level has been observed before using two-photon excitation,$^9$ but as yet no report has been made of the transition to the $v'=1$ level with multiphoton excitation. Also shown in Fig. 2 are the simultaneous excitations of the $v'=1$ level for linearly and circularly polarized photons. These simulations have been made on the basis of the rotational constants of the $C^1\Sigma^+$ state reported in Ref. 19, the rotational line strengths for three-photon transitions given in Ref. 15, and a rotational temperature in the ground state of the molecule of 13 K. The linearly polarized excitation spectrum has been simulated using only the first rank component of the hyperpolarizability tensor. Though the experimental excitation spectrum is in principle built up from the contributions of the first and third rank component, the contribution of the latter component is negligibly small compared to that of the former one as will be shown below. The circularly polarized spectrum derives by theory, on the other hand, only from the third rank component.

Figure 2 shows that the excitation spectra obtained with linearly and circularly polarized light are considerably different. On the basis of selection rules for $1^2\Sigma^+ \rightarrow 1^\Sigma^+$, transitions using three-photon excitation, $N$, $P$, $R$, and $T$ rotational branches are allowed. In the linearly polarized excitation spectrum, however, only $P$ and $R$ rotational branches are observed, while the circularly polarized spectrum does show all four allowed rotational branches. Apart from the difference in the observed rotational branches, a large difference between the two spectra is also found in the signal intensity. For linearly polarized light the signal is very strong and caution needs to be taken not to saturate the transition and the detection system. For circularly polarized light, on the other hand, full laser intensity has to be employed to observe the resonances. The spectra shown in Fig. 2 have been obtained using an expansion of pure CO. Similar spectra, albeit at a lower rotational temperature, have been obtained with an expansion of 5% CO in He. For such a mixture, however, the transition to the $v'=1$ level using circularly polarized light could not be observed, underlining the weakness of these signals.

When we compare the simulated excitation spectra of the $C^1\Sigma^+(v'=1)$ level with those obtained experimentally, excellent agreement is found for the spectrum measured with linearly polarized light. This agreement is somewhat poorer for the spectrum obtained with circularly polarized light. In particular, in the experimental spectrum the $R(0)$ and $P(1)$ lines are still present, which, on the basis of selection rules, should be absent. The reason for this is, of course, the signal arising from the first and third rank component of the hyperpolarizability tensor. Though the experimental excitation spectrum has been simulated using only the first rank component of the hyperpolarizability tensor, the magnitude of the latter component is negligibly small compared to that of the former one as will be shown below. The circularly polarized spectrum derives by theory, on the other hand, only from the third rank component.

The transition to the $v'=2$ level of the $E^1\Pi$ state [Figs. 3(g) and 3(h)] is located in an energy region in which the rotational transitions can also occur to the $A^1\Pi(v'=0)$ level, albeit at the two-photon level. The $S$ branch of the latter transition can be observed in Figs. 3(g) and 3(h), in which it is indicated as $S'$. Apart from the transitions to the $E^1\Pi(v'=2)$ and $A^1\Pi(v'=0)$ levels, Figs. 3(g) and 3(h) contain also resonances, marked with an asterisk, which can not be assigned to either one of these two states. As yet the origin of these transitions is not known, but since they do not derive from transitions to the electronic states of interest in the present study, we will not be concerned with them.

When the excitation spectra of the $v'=0$ level of the $E^1\Pi$ state are considered, we notice that for linear polarization only the $P$, $Q$, and $R$ branches are present. Changing the polarization from linear to circular results in an excitation spectrum in which the $P$, $Q$, and $K$ branches still strongly dominate the excitation spectrum, but in which now also extremely weak $O$ and $T$ branches can be observed. It can therefore be concluded that the contribution of the third rank component of the hyperpolarizability tensor is considerably smaller for excitation to the $v'=0$ level of the $E^1\Pi$ state than for excitation to the $v'=0$ and 1 levels of the $C^1\Sigma^+$ state. In other words, if $\sigma_{III}$ is defined as the signal intensity of a three-photon transition with contributions from both the first and third rank components with linearly polarized light, and $\sigma_{II}$ as the signal intensity of the same transition under identical circumstances with circularly polarized light (but vide infra), then the ratio $\sigma_{III}/\sigma_{II}$ would be substantially larger for the $v'=0$ level of the $E^1\Pi$ state than for the $v'=0$ and 1 levels of the $C^1\Sigma^+$ state. Consideration of the excitation spectrum of the $v'=1$ level of the $E^1\Pi$ state, on the other hand, shows that this
FIG. 2. (3+1) REMPI excitation spectra of the $C^1\Sigma^+$ state. (a) Experimental excitation spectrum of the $C^1\Sigma^+ (v'=0) \rightarrow X^1\Sigma^+ (v''=0)$ transition using linearly polarized light. (b) Experimental excitation spectrum of the $C^1\Sigma^+ (v'=0) \rightarrow X^1\Sigma^+ (v''=0)$ transition using circularly polarized light. (c) Experimental excitation spectrum of the $C^1\Sigma^+ (v'=1) \rightarrow X^1\Sigma^+ (v''=0)$ transition using linearly polarized light. (d) Experimental excitation spectrum of the $C^1\Sigma^+ (v'=1) \rightarrow X^1\Sigma^+ (v''=0)$ transition using circularly polarized light. (e) Simulated excitation spectrum of the $C^1\Sigma^+ (v'=1) \rightarrow X^1\Sigma^+ (v''=0)$ transition for linearly polarized light. (f) Simulated excitation spectrum of the $C^1\Sigma^+ (v'=1) \rightarrow X^1\Sigma^+ (v''=0)$ transition for circularly polarized light.
FIG. 3. (3+1) REMPI excitation spectra of the $E^1 \Pi$ state. (a) Experimental excitation spectrum of the $E^1 \Pi(v'=0) \rightarrow X^1 \Sigma^+(v''=0)$ transition using linearly polarized light. (b) Experimental excitation spectrum of the $E^1 \Pi(v'=0) \rightarrow X^1 \Sigma^+(v''=0)$ transition using circularly polarized light. (c) Experimental excitation spectrum of the $E^1 \Pi(v'=1) \rightarrow X^1 \Sigma^+(v''=0)$ transition using linearly polarized light. (d) Experimental excitation spectrum of the $E^1 \Pi(v'=1) \rightarrow X^1 \Sigma^+(v''=0)$ transition using circularly polarized light. (e) Simulated excitation spectrum of the $E^1 \Pi(v'=1) \rightarrow X^1 \Sigma^+(v''=0)$ transition for linearly polarized light. (f) Simulated excitation spectrum of the $E^1 \Pi(v'=1) \rightarrow X^1 \Sigma^+(v''=0)$ transition for circularly polarized light. (g) Experimental excitation spectrum of the $E^1 \Pi(v'=2) \rightarrow X^1 \Sigma^+(v''=0)$ transition using linearly polarized light. (h) Experimental excitation spectrum of the $E^1 \Pi(v'=2) \rightarrow X^1 \Sigma^+(v''=0)$ transition using circularly polarized light.
level exhibits a strikingly different polarization behavior from the $v'=0$ level. Though the use of linearly polarized light again results in the dominance of the $P$, $Q$, and $R$ branches, similar to what is observed for the $v'=0$ level, the circularly polarized excitation spectrum shows $O$, $S$, and $T$ branches of similar intensity as the $P$, $Q$, and $R$ branches. This implies a significant decrease of the ratio $\sigma_{III}/\sigma_{I\infty}$ for the $v'=1$ level as compared to the $v'=0$ level. A similar decrease can also be concluded from the excitation spectra of the $v'=2$ level. Here the linearly polarized excitation spectrum already contains $S$ and $T$ branches of similar intensity as the $R$ branch. The rotational lines of the $O$ and $N$ branches cannot be observed in these spectra because they are overlapped by the much stronger transitions to the $A^1\Pi$ state.

Good agreement is found between the simulated and experimental excitation spectra of the $E^1\Pi (v'=1)$ level. For this transition selection rules would forbid the $R(0)$ transition for circularly polarized light. Due to the less than 100% quality of the polarization this line is still observed in the experiment, albeit with a low intensity.

Figure 4 shows the rotationally resolved $(3+3)$ REMPI spectrum for the $A^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition using linearly and circularly polarized light. Though this transition has been studied previously with three-photon excitation, using ion and fluorescence detection, no measurements with circularly polarized light, nor of the ratio $\sigma_{III}/\sigma_{I\infty}$ have been reported. When linearly polarized excitation light is used, the excitation spectrum is dominated by the $P$, $Q$, and $R$ rotational branches. Circularly polarized excitation light does not change the excitation spectrum significantly; only a very weak $T$ branch is now present as well. The polarization behavior of the $A^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition, consequently, closely resembles what is observed for the $E^1\Pi (v'=0) \rightarrow X^1\Sigma^+ (v''=0)$ transition.

In order to obtain information on the three-photon excitation routes in the transitions discussed above, we need to determine the relative contributions of the first and third rank components of the hyperpolarizability tensor. The spectra shown in Figs. 2–4 demonstrate that there are two problems associated with the determination of the polarization ratio $\sigma_{III}/\sigma_{I\infty}$. First, except for the $E^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition, the contribution of the first rank component is so much larger than the contribution of the third rank component that the small ellipticity of our circularly polarized light results in relatively large signals deriving from the former component. A determination of $\sigma_{III}/\sigma_{I\infty}$ for the $R(1)$, for example, under the present experimental circumstances would lead to an underestimation of this ratio. We have therefore used rotational lines of different rotational branches. As a measure of $\sigma_{I\infty}$ the signal of the rotational lines of the $T$ branch has been measured. These transitions have only a contribution from the third rank component and their intensity is modulated by a polarization factor of 2.5. The small ellipticity of the circularly polarized light, consequently, does not influence their intensity significantly. As a measure of $\sigma_{III}$ we have, on the other hand, used the signal strength of the rotational lines of the $P$ and $R$ branches. These lines are not influenced significantly by a small ellipticity of linearly polarized light since the first rank contribution is several orders larger than the third rank contribution. Such measurements have been performed on pairs of rotational transitions, which have the same rotational level in the ground state in common, e.g., $[P(1),T(1)]$, $[P(2),T(2)]$, $[R(1),T(1)]$ etc. In this way the population distribution over the rotational levels of the ground state is not relevant. Use of the well-known three-photon rotational line strengths subsequently enables the determination of $\sigma_{III}/\sigma_{I\infty}$.

The second difficulty arises from the huge difference in signal intensity for linearly and circularly polarized light, except for the $E^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition. Measurements with circularly polarized light necessarily need to be performed with full laser power. Ideally, we would like to perform our measurements with linearly polarized light under the same conditions. When linearly po-

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**FIG. 4.** $(3+3)$ REMPI excitation spectra of the $A^1\Pi$ state. (a) Experimental excitation spectrum of the $A^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition using linearly polarized light. (b) Experimental excitation spectrum of the $A^1\Pi (v'=2) \rightarrow X^1\Sigma^+ (v''=0)$ transition using circularly polarized light.
polarized light is employed, however, such laser intensities lead to saturation of the detection system and the transition itself. We consequently had to use different laser intensities for measurements with linear and circular polarization, and determine the scaling factor for this difference in intensities. In order to accomplish this, we have first investigated for which laser intensities the $P$, $Q$, and $R$ lines are not saturated. This could easily be checked since their polarization dependence should in such a case show a $\cos^2 \Theta$ dependence, where $\Theta=0$ corresponds to linearity and $\Theta=\pi/2$ to circularly polarized light. An example of such behavior is given in Fig. 5. Within the intensity region, in which the transition was found not to be saturated, the intensity dependence of the signals has been determined. From this dependence the scaling factor could be obtained.

The ratio $\tau$ (vide infra), which is a measure for $\sigma_{II}/\sigma_{ec}$, obtained in this way is given in Table I for the transitions studied. Since the above mentioned problems are not encountered for the $E'\Pi (\nu'=2) \rightarrow X'\Sigma^+ (\nu''=0)$ transition, we have determined the ratio $\tau$ for this transition also using single rotational lines of the $R$ branch. The value obtained in this way has been found to be in good agreement with the value obtained according to the method described above. As mentioned before, the measurements have at first been performed on pure CO expansions. To make sure that there is no influence of possible dimers, such ratios have been determined as well with expansions of 5% CO in He. Since the signal intensities of the transitions are much reduced under such circumstances, these measurements could only be performed for the $\nu'=0$ level of the $C'\Sigma^+$ and the $\nu'=0$ and 2 levels of the $E'\Pi$ state. Here ratios $\tau$ have been obtained that, within experimental error, are the same as those found in pure CO expansions.

IV. DISCUSSION

The results given above have shown that for all but one of the states investigated a relatively large polarization ratio $\sigma_{II}/\sigma_{ec}$ is found. In the following we will assume that this ratio is determined by the three-photon excitation step. It has been shown before that such an assumption is valid as long as the ionization step is saturated and the excitation process is the limiting step. For the transitions to the $C'\Sigma^+$ and the $E'\Pi$ state this condition is fulfilled, but it might seem doubtful whether this is also true for (3+1) ionization via the $A'\Pi$ state. Previously, three-photon linearly polarized excitation spectra of the $A'\Pi$ state have been obtained by monitoring the fluorescence. Such spectra are not subject to the above mentioned restriction. Also in these spectra only the $P$, $Q$, and $R$ branches could be observed, from which it can be concluded that $\sigma_{II}/\sigma_{ec}$ is large, in agreement with the present results. We will therefore cautiously assume that our measured value of $\tau^2$ gives at least an indication of the correct order of magnitude for this quantity.

In order to reach a more detailed interpretation of the polarization ratios, we will compare them with the values expected for single-route transitions. Simultaneously, the theoretical description of three-photon transitions will be used to extract the relative contributions of the various routes for transitions which take place via more than one route. The results will finally be interpreted in terms of the electronic character of the states investigated.

For the theoretical description of three-photon absorption we will use expressions derived by Mainos et al. Other similar descriptions have been given by other authors, though several similar descriptions have been given by other authors, though several similar descriptions have been given by other authors, Though several similar descriptions have been given by other authors, the one of Mainos et al. is the present purposes the most suitable. According to these authors the rotational line strength of a three-photon electric dipole allowed transition between the ground state $|g\rangle$ and a final state $|f\rangle$ can be expressed as

$$S_{gf}(J_g; J_f) = \sum_{k=1,3}^3 \left| \langle \beta_{3k}^{(3)} | (2k+1) \Theta_{3k}^{(3)} (J_g; J_f) \right|^2 \sum_{\alpha} B_{3k}^{(3)} (\alpha) T^{(3)} (\alpha) \right| \right|^2$$

*See Eqs. (5a) and (5b) for definitions of $\tau^2$ and $\gamma$. 
where \( T^{(3)}(\alpha) = -\sum_{P_2(a)} T^{(3)}(q_1, q_2, q_3) \) and \( \Sigma \) represents a sum over all possible permutations \( q_1, q_2, q_3 \) within the route \( \alpha = q_1, q_2, q_3 \). In these expressions \( q_i \) can take the values 0, ±1, corresponding to the three spherical tensor components of the electric dipole moment of the \( i \)th absorbed photon with \( q_1 + q_2 + q_3 = \Delta \lambda \). The polarization dependence is contained in the factor \( |\beta^{(3)}_{\Delta \lambda}\\|^2 \) which is equal to \((2k+1)/3!\) for linearly polarized photons (\( \mu = 0 \)). For circularly polarized photons (\( \mu = ±1 \)) \( |\beta^{(3)}_{\Delta \lambda}\\|^2 \) is equal to 0 and \( |\beta^{(3)}_{\Delta \lambda}\\|^2 \) is equal to 35. The rotational line strength for a three-photon transition \( J_g \rightarrow J_f \) is represented by \( \Theta^{(3)}_{\Delta \lambda}(J_g; J_f) \) whose values are well-known. The quantity \( B^{(3)}_{\Delta \lambda} \) gives information on the relative weighting of the molecular routes in the rotational structure and can be explicitly calculated.

This quantity is not easily calculated and is consequently the only unknown in Eq. (1).

Let us now consider the possible routes for the three-photon excitation of the states, considered in the present study, i.e., the \( \Sigma \) and \( \Pi \) states. For a \( \Sigma \) state the possible routes turn out to be \((0,0,0)\), i.e., three parallel one-photon transitions, and \((0,−1,+1)\), i.e., one parallel and two perpendicular one-photon transitions. Although only one combination has been written here, it should be kept in mind that all possible permutations are allowed as well, and are, indeed, ultimately part of Eq. (1) via the expression for \( T^{(3)}(\alpha) \).

Now that we have established the routes via which three-photon excitation can take place to a \( \Sigma \) and \( \Pi \) state, we can calculate from Eq. (1) the expected polarization behavior for excitation via various routes. Since for both states only two routes are possible, we will in the following use the label 1 for one of the routes and 2 for the other route. In our experiments we have measured the polarization behavior by consideration of two different rotational transitions with the same ground state rotational level \( J_g \) in common. These transitions gave rise to signal intensities \( S^{(\Sigma)}_{gf}(J_g; J_f) \) for the transition measured with linearly polarized light and \( S^{(\Pi)}_{gf}(J_g; J_f) \) for the transition measured with circularly polarized light. According to Eq. (1) these rotational line strengths can be expressed as

\[
\begin{align*}
S^{(\Sigma)}_{gf}(J_g; J_f) & = \frac{1}{3} \Theta^{(3)}_{\Delta \lambda}(J_g; J_f) |B^{(3)}_{\Delta \lambda}(1) T^{(3)}(1) + B^{(3)}_{\Delta \lambda}(2) T^{(3)}(2)|^2 + 2 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f) |B^{(3)}_{\Delta \lambda}(1) T^{(3)}(1) + 2 B^{(3)}_{\Delta \lambda}(2) T^{(3)}(2)|^2, \\
S^{(\Pi)}_{gf}(J_g; J_f) & = 5 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f) |B^{(3)}_{\Delta \lambda}(1) T^{(3)}(1) + B^{(3)}_{\Delta \lambda}(2) T^{(3)}(2)|^2.
\end{align*}
\]

Equation (3) implies that the ratio \( S^{(\Sigma)}_{gf}(J_g; J_f)/S^{(\Pi)}_{gf}(J_g; J_f) \) is obtained as

\[
\begin{align*}
\frac{S^{(\Sigma)}_{gf}(J_g; J_f)}{S^{(\Pi)}_{gf}(J_g; J_f)} & = \frac{\Theta^{(3)}_{\Delta \lambda}(J_g; J_f)}{5 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f)} \left| \frac{B^{(3)}_{\Delta \lambda}(1) T^{(3)}(1)}{B^{(3)}_{\Delta \lambda}(2) T^{(3)}(2)} \right|^2 + \frac{2 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f)}{5 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f)} \left| \frac{B^{(3)}_{\Delta \lambda}(1) T^{(3)}(1)}{B^{(3)}_{\Delta \lambda}(2) T^{(3)}(2)} \right|^2 \frac{5 \Theta^{(3)}_{\Delta \lambda}(J_g; J_f)}{S^{(\Pi)}_{gf}(J_g; J_f)}.
\end{align*}
\]

From Eq. (4) a quantity \( \gamma \) can be derived, which is independent of the used rotational transitions, and which would be a measure for \( \sigma_{lin}/\sigma_{circ} \) if the same rotational transition would have been studied with linearly and circularly polarized light

\[
\gamma = \frac{|B^{(3)}_{\Delta \lambda}(1)|^2 + |B^{(3)}_{\Delta \lambda}(2)|^2}{|B^{(3)}_{\Delta \lambda}(1)|^2 + |B^{(3)}_{\Delta \lambda}(2)|^2}.
\]
A \( \Sigma \) state is rather limited and only becomes important if a \( \Pi \) state (vide infra) allows us to conclude that \( \Sigma \) states cannot be considered as being dominated by a \( \Pi \) state and the vibrational levels of the \( \Sigma \) state by an almost equal participation of the two possible excitations, which gives contributions of the same order of magnitude to the results from the excitation to the \( \Sigma \) orbital, which is to a large extent determined by the preferred excitation route. The excitation energy of this state is reasonably close to two-thirds of the excitation energies of the \( \Sigma \) and \( \Pi \) states\(^{\text{24}} \) and its electron configuration is such that the same electron is excited as in the \( \Sigma \) and \( \Pi \) states. This would imply that the excitation routes \((0,-1,+1)\) and \((0,0,+1)\), respectively, would dominate.

Such expectations are only borne out nicely for the \( \nu'=2 \) level of the \( \Sigma \) state. As is observed in Figs. 3(g) and 3(h), excitation of this state results in a near-resonance with the \( \Pi \) state at the two-photon level and the polarization behavior demonstrates accordingly a dominance of the \((0,0,+1)\) excitation route. Surprisingly, excitation of the other vibrational levels of the \( \Sigma \) state and the vibrational levels of the \( \Pi \) state does not result in a similar dominance, but is characterized by an almost equal participation of the two possible excitation routes. It therefore seems that the influence of the \( \Pi \) state is rather limited and only becomes important under (near)-resonance conditions.

The above analysis has been performed from a molecular point of view and has shown that the three photon transitions to the \( \nu'=2 \) level of the \( \Sigma \) state is only valid for the \( \Sigma \) (\( \nu'=3 \)) level, it is clear from Figs. 2 and 3 and Table I that the polarization behavior of the other transitions is not equal. In this respect it is especially the transition to the \( \Sigma \) (\( \nu'=1 \)) state, which deserves further attention. As has been remarked before, the polarization behavior of the transitions to the \( \nu'=1 \) level shows a similar value of \( \gamma \) and the experimental values are finite, but orders of magnitude larger than the theoretical values for a molecular single-route excitation. It would therefore appear that the atomic picture is in good agreement with the observed polarization behavior, or, vice versa, that the polarization behavior of the transitions confirms their localized nature in three-photon excitation.

Even though we have concluded that the single-route excitation picture is only valid for the \( \Sigma \) (\( \nu'=3 \)) level, it is clear from Figs. 2 and 3 and Table I that the polarization behavior of the other transitions is not equal. In this respect it is especially the transition to the \( \Sigma \) (\( \nu'=1 \)) state, which shows a similar value of \( \gamma \) and the experimental values are finite, but orders of magnitude larger than the theoretical values for a molecular single-route excitation. It would therefore appear that the atomic picture is in good agreement with the observed polarization behavior, or, vice versa, that the polarization behavior of the transitions confirms their localized nature in three-photon excitation.

For an explanation of this difference two observations are of importance. First, if it is assumed that the atomic orbital picture is valid, we would conclude that the \( \Sigma \) (\( \nu'=1 \)) level demonstrates an anomalous polarization behavior. This is supported in part by our results obtained for the \( \Pi \) (\( \nu'=2 \)) level, which shows a similar value of \( \gamma \) as the \( \Sigma \) (\( \nu'=0 \)) level, though we hasten to point out that the former value might be off by an order of magnitude from the true value (vide supra). Second, in the molecular orbital picture it might be argued that the difference between the two vibrational levels arises from the difference in excitation wavelength. This energy difference might ultimately lead to different \( \gamma \) contributions for the two levels. Such a large dependence might indeed be expected if a (near-)resonance occurs at the one- or two-photon level as has been observed in the present study for the \( \Sigma \) (\( \nu'=2 \)) level, but such a (near-)resonance does not occur for the \( \nu'=1 \) level. Such a large excitation energy dependence is also considered unlikely on the basis of our observations.
results on the $C^1\Sigma^+$ state. Here the two-photon levels in the three-photon excitation of the $\nu' = 0$ and 1 levels are located $\sim 3460$ and $\sim 2020$ cm$^{-1}$, respectively, below the $A^1\Pi(\nu' = 0)$ state. This energy shift does not result in significant changes in the polarization behavior. The analogous levels in the excitation of the $\nu' = 0$ and 1 levels of the $E^1\Pi$ state are 2780 and 1340 cm$^{-1}$ below the $A^1\Pi(\nu' = 0)$ state. In view of the energy independence of the polarization behavior on reducing the energy difference with the $A^1\Pi(\nu' = 0)$ state from 3460 to 2020 cm$^{-1}$, it is hard to believe that reducing the energy difference from 2780 to 1340 cm$^{-1}$ would be able to change the polarization behavior so dramatically.

A possible explanation for our observations, and one that we prefer, might be that the electronic character associated with the $\nu' = 1$ level is slightly different from that of the $\nu' = 0$ level. A priori we can conclude that this difference is relatively small, since other spectroscopic properties of the $\nu' = 1$ level, such as the transition strength and the rotational constants, do not show significant deviations from their expected values.\textsuperscript{1-3} It is only by virtue of the fact that the $\nu' = 0$ level has such a large value of $\pi$ that small perturbations can become so much amplified.

Kirby and Cooper have previously calculated the potential energy surface of a number of $1\Pi$ states in CO.\textsuperscript{26} From their results the $E^1\Pi$ state appears to have a single minimum but the potential is nonetheless unusual. At 2.65 bohr, close to the equilibrium distance of 2.14 bohr and at an energy of $\sim 8000$ cm$^{-1}$ above the energy minimum, the potential flattens off, while at 3.3 bohr an avoided crossing takes place with the $3\Pi$ state,\textsuperscript{28} which is the first member of the Rydberg series converging to the second ionic limit. Reflective of the changes in the potential are the changes in the electronic character of the $E^1\Pi$ state as a function of the internuclear distance: around its equilibrium value it is the electronic character of the $\nu' = 0$ level. A priori we can conclude that this difference is relatively small, since other spectroscopic properties of the $\nu' = 1$ level, such as the transition strength and the rotational constants, do not show significant deviations from their expected values.\textsuperscript{1-3} It is only by virtue of the fact that the $\nu' = 0$ level has such a large value of $\pi$ that small perturbations can become so much amplified.

V. CONCLUSIONS

We have studied the three-photon excitation of the $C^1\Sigma^+$, the $E^1\Pi$, and, for comparison, the $A^1\Pi$ state of CO with REMPI spectroscopy. Using circularly polarized light we have been able to observe for the first time very weak rotational transitions corresponding to $\Delta J = \pm 2$ and $\pm 3$, allowing for a determination of the polarization ratio $\sigma_{\Pi,\Pi}/\sigma_{\Pi,\Sigma}$. Analysis of these results within the single route approximation has revealed that this approximation is not valid for all but one of the transitions investigated in the present study. Application of the theoretical description of three-photon absorption has enabled the calculation of the relative contributions of the two interfering routes. It has been shown that the polarization behavior of the transitions can also be explained satisfactorily in a picture in which the excitations are considered as predominantly atomic excitations, thereby indicating their localized nature for three-photon excitation. Finally, a large difference has been observed in the polarization behavior of the $\nu' = 0$ and 1 vibrational levels of the $E^1\Pi$ state. This has been taken as evidence for a slightly different electronic character of these two vibrational levels.

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