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MULTIPHOTON ROTATIONAL SPECTROSCOPY OF THE NO MOLECULE: POLARIZATION EFFECTS IN THE FLUORESCENCE SPECTRUM COMPARED TO PHOTOIONIZATION, A WAY FOR DETERMINING THE CHANNELS TOWARDS IONIZATION

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The development of high power narrowband tunable pulsed lasers brings new investigation possibilities in the field of the optical spectroscopy of atoms and molecules. Although molecular spectroscopy is one of the research fields in science having been extensively studied, a variety of important aspects have been demonstrated very recently in this field as radiation sources have been improved. Here, we intend to discuss polarization effects on the intensities of multiphoton excited rotational lines of simple molecules. Let us first recall the principles which govern these effects.

In one-photon transitions the Born-Oppenheimer and Franck-Condon principles allow a complete treatment and separation of the dynamics into rotational and vibronic parts since in this case there is only one possible value for the quantum number \( k \) of the transfered angular momentum \( k \), this is \( k = 1 \), whereas the absorption of a photon will change the total angular momentum by 0 or \( \pm 1 \) regardless of the incident polarization. The fact that there is only one value for \( k \) will permit one to obtain measurements on the relative rotational line intensities of one-photon transitions without specifying the vibronic part.

However, in multiphoton transitions, the transfer of angular momentum from the laser beam to the molecule is realized through absorption of more than one photon. For the \( n \)-order dipole process, the change in total angular momentum must be \( \leq n \) since the absorption of each photon can alter the angular momentum by 0 or \( \pm 1 \). Instead the one-photon transitions, now the quantum number \( k \) for the transfered angular momentum can take more than one value, each value for the quantum number \( k \) will couple the rotational and vibronic part. Therefore, since the intensity of a rotational line in a multiphoton transition generally may have one contribution from each quantum number \( k \) and the corresponding vibronic parts are different, we are not able to separate the rotational line strength into a rotational and a vibronic part.

Consequently, in a multiphoton transition, there is a number of unknown vibronic constants which is equal to the possible values for the quantum number \( k \). To each value of \( k \), we have a \( k \)-term which may contribute to the intensity of a rotational line. The change in the total angular momentum can be 0, \( \pm 1 \), \( \pm 2 \), ..., \( \pm k \) whereas the contribution of the \( k \)-term to a rotational line must satisfy selection rules which assure the angular momentum conservation of multiphoton process.

Although the multiphoton rotational line factors are explicitely known, the vibronic constants are not, this renders incomplete the expression for the total rotational line strength and thus one is unable to compare rotational line intensities predicted by theory with those obtained by the experiment. Our work intends to fill this gap.

Theoretical:

According to our calculations, let us briefly recall that the rotational line strength (RLS) in the electric dipole approximation of a \( n \)-photon transition between an initial state \( g \) and a final state \( f \), will lead to a decomposition of the rotational structure into a sum of contributions.
\[ S(n, \gamma) = \beta_{k, np}(n) \left( \gamma^2 \sum_{k} \frac{\beta_{k, \Delta \lambda}^{(n)}}{2k + 1} \right), \]

Explanation:

\( \beta_{k, np}(n) \) is a constant which depends on the polarization and the number of absorbed photons and gives the relative weighting of the contribution of the k-term. \( p = 0 \) stands for linearly polarized photons while \( p = \pm 1 \) hold for circularly polarized photons, the sense of the polarization in the circular case has no any effect on this constant. The polarization vector \( \mathbf{e} \) is defined in the space fixed frame (SFF) and we suppose that all the absorbed photons have the same energy and polarization state.

\( \beta_{k, \Delta \lambda}^{(n)} \) is the rotational line factor which contains the rotational dependence of the (RLS) and the coupling case of the initial and final states. Explicit forms for the rotational line factors of any spin-multiplicity have been presented in previous works, they hold for transitions between two states which both belong to Hund's case (a) or case (b), as well as, for transitions between a state with a case (a) coupling and a state with case (b) coupling. Generally, the molecular states may have any coupling intermediate between (a) and (b).

The vibronic dependence of the (RLS) is contained in the quantity \( \beta_{k, \Delta \lambda}^{(n)} \) which is coupled with the rotational line factor and the polarization constant \( \beta \) through the quantum number \( k \) of the absorbed photon angular momentum \( \hbar k \), the above quantities vanish when \( k < \Delta \lambda \) or \( k < |np| \). Angular momentum conservation arguments show that the possible values of the quantum number \( k \) are \( n, n - 2, n - 4, \ldots \), \( |\Delta \lambda| \) if \( n - |\Delta \lambda| \) is even or, \( |\Delta \lambda| + 1 \) if \( n - |\Delta \lambda| \) is odd. The quantity \( T(n) \) includes summation over sets defined by the couple \( (n, \Delta \lambda) \) and each characterizes a precise multiphoton pathway which can be traced within the molecule following symmetry considerations and selection rules. The presence of real molecules states plays the role of virtual intermediate states in the overall multiphoton process. We intend to present now some preliminary results which conform the validity of our theoretical assumptions.

**Experimental**: The two photon spectrum of NO

Briefly, the third harmonic output of a Quantel NdYag laser is sent in a grazing incidence design dye laser with amplifier stage. Polarization of light is achieved by an intracavity glan polarizer. The output of the amplifier stage travels through a glan analyzer followed by a Fresnel rhomb hence producing either linearly a circularly polarized photons. The beam is focused into a fluorescence (TPEF) or ionization (MPI) cell. Fluorescence light is viewed at 90° by the photomultiplier through a H-20 F/4.2 Jobin-Yvon monochromator. Both TPEF or MPI signal and the incident laser power are digitized with a PAR Boxcar integrator or a Keithley electrometer and passed to a P1600 Logabax computer for storage and processing.

**Results**: Two photon rotational line structure for the \( A \ 2^\Xi^+(v'=0) - X \ 2\Pi(v''=0) \) gamma band of nitric oxide.

In such a case, this is the first molecular excited state hence there are no resonant intermediate excited state. Then, the RLS will be proportional to the \( \beta_{k, \Delta \lambda}^{(n)} \) term of our theoretical expression multiplied by the Boltzmann factor. Fig. 1a and b exhibit the predicted and experimental two photon excitation spectra in the NOY(0,0) 0\_2 branch. The synthetic intensities have been deduced from the well known molecular constants of both states.

Fig. 1c exhibits the corresponding multiphoton spectrum.

Another interesting aspect lies in polarisation effects. From our theoretical expression of the RLS, one can deduce the ratio of the intensity of a rotational line with linearly polarized light over the intensity of the same line obtained from circularly polarized light. From this, it results that
We checked this ratio experimentally for the two photon excited Y band NO with a good agreement of 1.4 with respect to the theoretical value of 1.5.

\[ \sigma_n = \frac{\left( \frac{s_{fg}}{s_{fg\text{ circ}}} \right)}{\left( \frac{s_{fg}}{s_{fg\text{ circ}}} \right)} = \frac{|g_{n,0}|^2}{|g_{n,n}|^2} \]

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