

HIGH-RESOLUTION STUDY OF THE NO $E^2\Sigma^+ \leftarrow A^2\Sigma^+$ TRANSITION BY PULSED-cw DOUBLE RESONANCE

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A new experimental technique which combines the high power of a pulsed laser with the narrow bandwidth of a single mode cw laser has been used to study the NO($E^2\Sigma^+, v=0 \leftarrow A^2\Sigma^+, v=0$) transition under high resolution in a molecular beam. The spin-rotation splitting in the E state has been analyzed and shows the effect of a heterogeneous perturbation between the $E^2\Sigma^+, v=0$ and the $B^2\Pi, v=17$ state. Time-resolved E→A fluorescence spectra show residual effects of Rabi oscillations and can be correctly described using the optical Bloch equations for a two-level system, including radiative losses.

Various laser spectroscopic methods have been developed to study electronically excited states of atoms and molecules [1]. Single mode cw lasers in combination with Doppler-free techniques attain a spectral resolution of $1:10^9$, which means that an accuracy of about 1 MHz can be obtained in the visible and near UV region of the spectrum. This high resolution is needed when fine and hyperfine structure is studied, and to avoid spectral congestion, especially in larger molecules. High lying electronic states, connected to the electronic ground state by transitions in the far UV, are difficult to reach with cw lasers. Narrow bandwidth cw radiation sources are not available in this frequency region, and only in favourable cases two-photon transitions can be induced [2].

Pulsed lasers on the other hand can produce intense tunable radiation ranging into the XUV. The high peak powers allow the efficient use of one-photon excitation or multiphoton pumping schemes to reach high lying electronic states. It is often the relative large bandwidth of the pulsed laser which sets the lower limit for the spectral resolution.

Here we report a new double resonance technique in which full advantage of the specific properties of both a pulsed and a cw laser is taken. The pulsed laser is used for efficient excitation of molecules in a continuous molecular beam out of the electronic ground state to an electronically excited state. A narrow

bandwidth cw laser is used to pump the molecules higher up, and *both* electronic states connected by the cw laser can then be studied under high resolution. Combining a pulsed laser with a cw laser will give quite a large loss in duty cycle. The exact magnitude of this loss factor depends on the experimental set-up (length of the interaction region) as well as on the lifetime of the intermediate electronic state. The efficient excitation by the pulsed laser together with the application of time-resolved detection techniques compensates to a large extent for this loss factor.

In our set-up a collimated continuous beam of NO molecules is intersected perpendicularly by pulsed laser radiation around 226 nm and by single frequency cw laser radiation around 600 nm. Both beams are unfocused and have a circular cross section of 1 mm diameter at the molecular beam. Laser-induced fluorescence from the intersection region is imaged on a photomultiplier tube. The excitation scheme we applied is schematically given in fig. 1. Several mJ of 226 nm radiation in a 10 ns pulse is produced by frequency doubling the output of a XeF-excimer-laser-pumped pulsed dye laser, operating on coumarin 47, in a β -BaB₂O₄ (BBO) crystal. This radiation has a bandwidth of about 0.5 cm^{-1} and is used to induce the NO($A^2\Sigma^+, v=0 \leftarrow X^2\Pi, v=0$) transition. It is possible to populate single rotational levels of the $A^2\Sigma^+, v=0$ state; this is controlled by

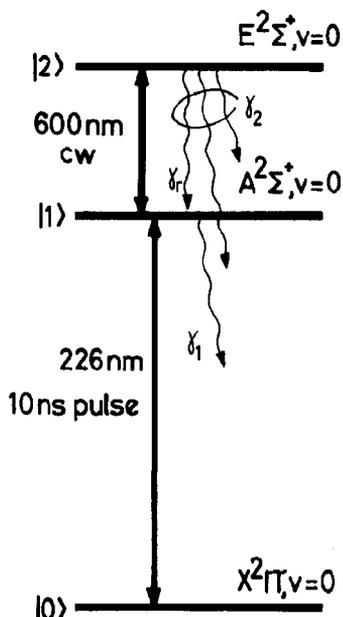


Fig. 1. Schematic representation of the excitation process. The different loss processes out of both excited electronic states used in the description of the time-resolved fluorescence spectra are also indicated in the figure.

monitoring the resulting A \rightarrow X fluorescence. Narrow bandwidth cw laser radiation (≤ 0.3 MHz) at 600 nm is obtained from an Ar-ion-laser-pumped ring dye laser operating on R 6G. During their radiative lifetime of about 208 ns [3] the NO(A $^2\Sigma^+$, $v=0$) molecules can be excited with the cw radiation to the E $^2\Sigma^+$, $v=0$ state. Both total and time-resolved E \rightarrow A double resonance fluorescence are simultaneously detected using a boxcar integrator with typically a 500 ns gate width and a digital oscilloscope. Although this fluorescence is only a fraction of the total E-state fluorescence, it has the advantage that it can be measured against a zero background level by the use of cut-off filters.

A typical high resolution E \leftarrow A spectrum obtained by scanning the cw laser whereas the pulsed laser is kept fixed in frequency exciting both fine structure levels of the NO A $^2\Sigma^+$, $v=0$, $N=1$ level is shown in fig. 2. Linewidths and splittings are measured in terms of the distance between the transmission peaks of a temperature- and pressure-stabilized interferometer. The 17 MHz linewidth of a single resolved hyperfine transition is mainly determined by the residual Doppler broadening due to the divergence of

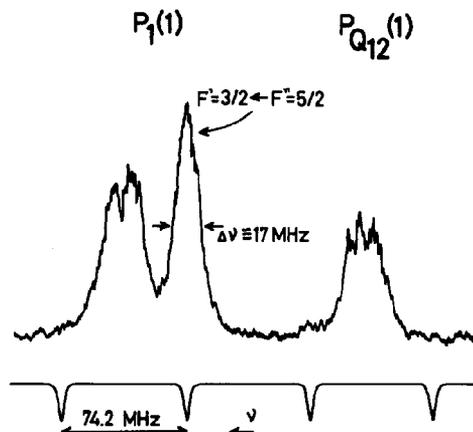


Fig. 2. Typical high-resolution spectrum of the NO(E $^2\Sigma^+$, $v=0$ \leftarrow A $^2\Sigma^+$, $v=0$) P $_1$ (1) and P $_{Q12}$ (1) transition. The pulsed laser is set on the Q $_1$ (1) and its satellite line of the A \leftarrow X transition, and simultaneously populates both fine structure levels. In the P $_1$ (1) transition the hyperfine structure is shown partly resolved. Time-resolved measurements are made on the single isolated hyperfine transition.

the molecular beam. To avoid power broadening only 4 mW of cw laser radiation is used in recording this spectrum. By allowing a somewhat larger beam divergence and using about 50 mW of cw laser power the linewidth increased to 25 MHz. With a repetition rate of the pulsed laser of 15 Hz and by averaging over 2 s (30 samples) a S/N of 1000 or better could then be obtained on the strongest lines in the double resonance spectrum.

A series of measurements have been performed to determine accurately the magnitude of the spin-rotation splitting in the E $^2\Sigma^+$, $v=0$ state. This splitting was too small to be resolved in Doppler-limited Fourier transform spectroscopy of electronic emission bands from the E state in the near IR [4]. The magnitude of the observed splitting is shown in fig. 3 as a function of the rotational quantum number N . For low N values the expected linear dependence on N is seen, yielding a value of $\gamma = -3.15 \pm 0.20$ MHz. A deviation from the straight line is observed between $N=13$ and $N=17$ and can be completely explained as a perturbation of the E $^2\Sigma^+$, $v=0$ by the B $^2\Pi$, $v=17$ state. At these N values equal J levels of both electronic states are less than 10 cm $^{-1}$ apart. It should be noted, however, that the E $^2\Sigma^+$ state is a 4s σ Rydberg state, differing in two electron orbitals from the $\pi^3\pi^2$ B $^2\Pi$ non-Rydberg state. Therefore, a

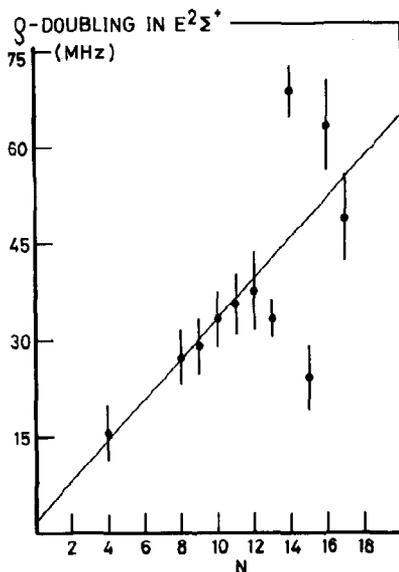


Fig. 3. Magnitude of the observed spin-rotation splitting in the $E^2\Sigma^+$, $v=0$ state as a function of the rotational quantum number N . As F_2 levels are higher in energy than F_1 levels the splitting is in fact negative. Between $N=13$ and $N=17$ the effect of the perturbation due to the $B^2\Pi$, $v=17$ state is seen.

coupling between these states via one-electron operators is not possible. The observed perturbation can be explained only due to configuration interaction [5], as will be discussed in more detail in a forthcoming paper [6]. The smallness of this perturbation explains why it escaped prior observation and explicitly demonstrates the merits of the high resolution we obtained.

The pulsed-cw double resonance technique also reveals dynamical properties of the electronically excited states. Time-resolved fluorescence from the E state reflects the evolution in time of the population of this state, that is coherently coupled to the A state by the cw laser. To measure this time-resolved fluorescence both lasers are kept fixed in frequency. The specific measurements we want to discuss here are made with the pulsed laser populating the $N=1$, $J=3/2$ level in the $A^2\Sigma^+$, $v=0$ state. The cw laser frequency is set on the top of the Doppler-broadened profile of the resolved $F=3/2 \leftarrow F=5/2$ hyperfine component of the $E \leftarrow A$ $P_1(1)$ transition, shown in fig. 2. In this case red fluorescence from one single hyperfine level of the E state is detected. Such a time-resolved spectrum, averaged over 100 samples and with 57 mW of cw laser power, is shown in fig. 4.

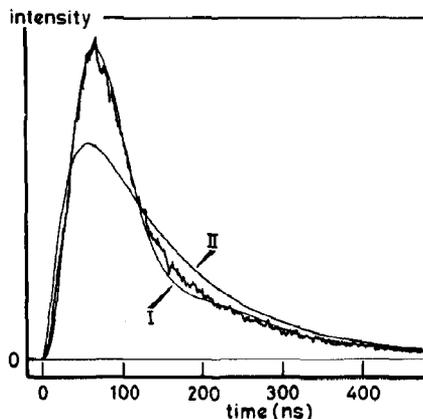


Fig. 4. Observed and simulated time-resolved fluorescence spectra. The cw laser induces the isolated hyperfine transition of $P_1(1)$ shown in fig. 2, with 57 mW of laser power. The simulation that follows from the Bloch equations, curve I, is seen to fit the experimental curve very well. Using the rate equation description yields a result, curve II, around which both the experimental and the "exact" theoretical curve show a Rabi oscillation.

These time-resolved spectra can be simulated for a coherently driven two-level system, including radiative losses out of both levels. The description of the NO(E-A) system as an isolated two-level system is justified by the fact that the pulsed laser is on for only 10 ns. In our model we assume that at a given time equal to zero a certain number of molecules is excited instantaneously to the A state whereas no molecules are assumed to be in the E state yet. The kinetic description of this system can be reduced to the Bloch equations for the components of the density matrix $\rho(t)$, ρ_{11} , ρ_{22} , $\tilde{\rho}_{12} = \rho_{12} \exp(i\Delta t)$ and $\tilde{\rho}_{21} = \rho_{21} \exp(-i\Delta t)$ as [7]

$$\begin{aligned} \dot{\rho}_{11} &= \frac{1}{2}iV(\tilde{\rho}_{12} - \tilde{\rho}_{21}) + \gamma_r\rho_{22} - \gamma_1\rho_{11}, \\ \dot{\rho}_{22} &= -\frac{1}{2}iV(\tilde{\rho}_{12} - \tilde{\rho}_{21}) - \gamma_r\rho_{22}, \\ \dot{\tilde{\rho}}_{12} &= \frac{1}{2}iV(\rho_{11} - \rho_{22}) - (\frac{1}{2}\gamma_1 + \frac{1}{2}\gamma_2 - i\Delta)\tilde{\rho}_{12}, \\ \dot{\tilde{\rho}}_{21} &= -\frac{1}{2}iV(\rho_{11} - \rho_{22}) - (\frac{1}{2}\gamma_1 + \frac{1}{2}\gamma_2 + i\Delta)\tilde{\rho}_{21}. \end{aligned} \quad (1)$$

In these equations V is the excitation rate and is proportional to the square root of the applied laser power, Δ is the mean frequency detuning $\omega_0 - \omega$ and γ_i ($i=1, 2$) is the radiative loss rate out of level i . The rate of spontaneous emission between the coupled hyperfine levels is indicated by γ_r . For our system the loss rate $\gamma_1 = 1/\tau_A = 4.8 \times 10^6 \text{ s}^{-1}$ is known [3] whereas we have measured $\gamma_2 = 1/\tau_E$ in another

double resonance experiment employing two pulsed lasers [6], yielding $\gamma_2 = 2.44 \times 10^7 \text{ s}^{-1}$. For the hyperfine transition we studied, the rate γ_r is 50% of the total E→A emission rate, which in its turn is estimated to be 50% of the total E-state emission rate γ_2 [8]. A value of $\gamma_r = 6.0 \times 10^6 \text{ s}^{-1}$ is derived in this way. The only parameter to be adjusted in eq. (1) is the excitation rate V . An independent determination of V is however possible from the plot of the total time-integrated double resonance signal intensity versus the applied cw laser power [6]. The system of four coupled differential equations is numerically solved for the case of excitation with a narrow bandwidth laser, set on the top of a Gaussian line profile of a single, isolated transition. A Doppler width of 25 MHz is taken. A small retarding effect of about 12 ns caused by the PMT we used is also taken into account in the simulated spectra. In fig. 4 the best fit to the experimental curve is shown (curve I). The parameter V was equal to $V = 3 \times 10^7 \text{ s}^{-1}$. The slight deviations between theory and experiment can be explained by the assumptions we made. First of all, not all molecules start at once in the A state as it takes several ns to populate this state. Secondly, we assume only one interaction parameter V , but due to the slight spatial variation of the cw laser power we should average over several values of V ; this would smear out, especially the dip around 160 ns, a little more. A similar effect is introduced if the two different transition strengths due to the degenerate M_F levels are taken into account, although this latter effect alone cannot be responsible for the small deviations observed.

If phase relaxation processes would be fast the off-

diagonal matrix elements of the density matrix would not vary significantly in time. In such a case $\dot{\rho}_{12}$ and $\dot{\rho}_{21}$ can be set equal to zero. This yields off-diagonal matrix elements that vary quasi-stationary in time and by which the above equations are reduced to the much simpler rate equation system [7]. In fig. 4 the time dependence of the E-state population in this rate equation approach is also shown (curve II). It is clearly seen that this latter approach is not correct in our case. A residual effect of Rabi oscillations is seen in both the experimental curve and the "exact" theoretical fit, which can never be explained using the rate equation description of the two-level system.

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