Dopplerfree Zeeman spectroscopy of the NO2 593.3 nm band

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Doppler-free Zeeman spectroscopy of the NO_2 593.3 nm band

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The visible absorption band of NO_2 has been the subject of great interest in the aspect of understanding the perturbation in the electronic excited state. It is known by numerous investigations that the vibrational, rotational, and spin levels are irregularly shifted, leading fairly complicated structure in the high-resolution spectrum.[1-3] The g-factor measurements by optical radio frequency double resonance[4] and Zeeman quantum beats[5] have revealed that the magnetic properties of the NO_2 molecules vary with the rotational and spin levels and are affected by the perturbations. In order to investigate the rotational and spin structure on the basis of the magnetic properties, we have studied Doppler-free Zeeman spectroscopy in a collimated molecular beam.[6,7]

A part of the fluorescence excitation spectrum of the NO_2 593.3 nm band and that in the external magnetic field of 205 G are shown in Fig. 1. At zero field, one can see well-resolved fine structure by an electron spin ($S=1/2$) and hyperfine structure by a nuclear spin of the N atom ($I=1$).[3,8] We found most of the observed rotational lines were split into many lines of magnetic sublevels in the weak magnetic field of 205 G, but the amplitude of the splitting was different with the rotational levels. The NO_2 molecule is bend (C_{2v}) both in the ground $^2A_1$ and the excited $^2B_2$ states, and is approximated by a prolate symmetric top with its principal a axis along the O–N–O bond. Two spin sublevels $F_1(J=N+1/2)$ and $F_2(J=N-1/2)$ are split by the spin–rotation interaction. The $^2B_2-{}^2A_1$ absorption is a parallel transition and the selection rules are $\Delta K=0$, $\Delta N=0$, ± 1, and $F_1 \leftrightarrow F_2$. Consequently, we denote each spectral line as, for example, $P_{K''}(N'')$ F_1 or F_2 for $\Delta N=-1$. We could easily assign prominent lines in the low N region using the reported molecular constants.[1,2]

It was clearly seen that the Zeeman splitting was remarkably large in the $|K'=0,\ N'=N''\pm 1\rangle \leftarrow |K''=0,\ N''\rangle$ line. In Fig. 2 are shown the expanded spectra of the $R_0(0)$ lines and the changes with the magnetic field. The energy levels of magnetic sublevels of a molecule in the magnetic field with the doublet spin state excluding the nuclear spin were theoretically investigated by Hougen.[9] Here we make similar consideration including the nuclear spin of the N atom ($I=1$). In the absence of the magnetic field, the nuclear spin **I** is coupled to the total angular momentum $\mathbf{J}=\mathbf{N}+\mathbf{S}$, where **N** is the total angular momentum excluding the electron spin **S**. Then, the wave function is well described as $|\alpha KNSJIFM_F\rangle$, where $\mathbf{F}=\mathbf{I}+\mathbf{J}$ and M_F is the projection along the laboratory-fixed Z axis. The allowed $\Delta F=0$, ± 1 transitions construct hyperfine structure at zero field. The hyperfine splitting is mainly attributed to the Fermi contact interaction, which is much larger in the $^2A_1$ state than $^2B_2$.[8] In the weak magnetic field, where the Zeeman term is smaller than the zero field splitting (ZFS) by the spin–rotation interaction $\gamma(N+1/2)$,[9] the nuclear spin is decoupled and the wave function is described as $|\alpha KNSJM_J\rangle|IM_I\rangle$. In the strong field, the electron spin is also decoupled and the wave function is changed to $|\alpha KNM_N\rangle|SM_S\rangle|IM_I\rangle$. The $R_0(0)$ line is the transition from the $|K''=0,\ N''=0\rangle$ level in the ground $^2A_1$ state to the $|K'=0,\ N'=1\rangle$ level in the excited $^2B_2$ state. We observed the Zeeman spectrum up to 290 G, where the Zeeman splitting is smaller than the ZFS ($\gamma'=-0.0483\ \mathrm{cm}^{-1}$) in the $^2B_2$ state, and each M_J sublevel is split into the triplet levels of $I=1$. However, in the $^2A_1$ state, the wave function is well described by the strong-field basis, because there is only the F_1 level and $M_J=M_S$ for $|K''=0,N''=0\rangle$. The $\Delta M_J=0$ or ± 1 transitions can be observed for the π or σ pump in which the magnetic field (**H**) is parallel or perpendicular to the electric vector (**E**) of the laser light, respectively. Therefore, a couple of triplet lines is observed in both the F_1 and F_2 lines for the π pump ($M_J=\pm 1/2 \leftarrow M_J=\pm 1/2$). For the σ pump, two couples of triplet lines are observed in the F_1 line ($M_J=\pm 3/2 \leftarrow M_J=\pm 1/2$, and $M_J=\pm 1/2 \leftarrow M_J=\mp 1/2$), but a couple of triplet lines are observed in the $R_0(0)$ F_2 line ($M_J=\pm 1/2 \leftarrow M_J=\mp 1/2$). We found the splittings and the intensities of the observed spectral lines were in good coincidence with the calculated ones by the diagonalization of the energy matrix including the spin–rotation, hyperfine, and Zeeman interactions with the g value of 2.0023 for both states. It is consistent with the

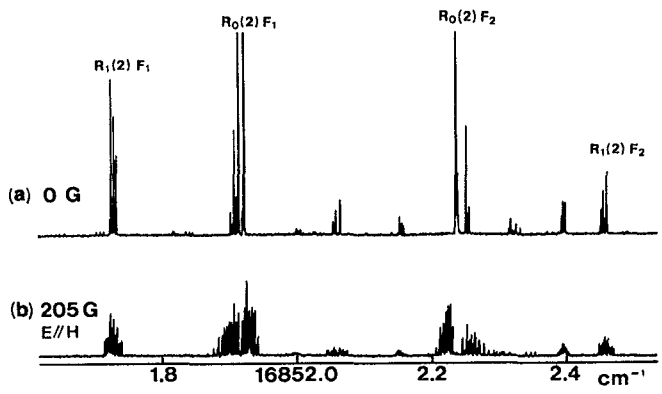

FIG. 1. Doppler-free fluorescence excitation spectrum of NO_2 (a) at zero field and (b) in the magnetic field of 205 G. The magnetic field (**H**) was applied parallel to the electric vector (**E**) of the laser light.

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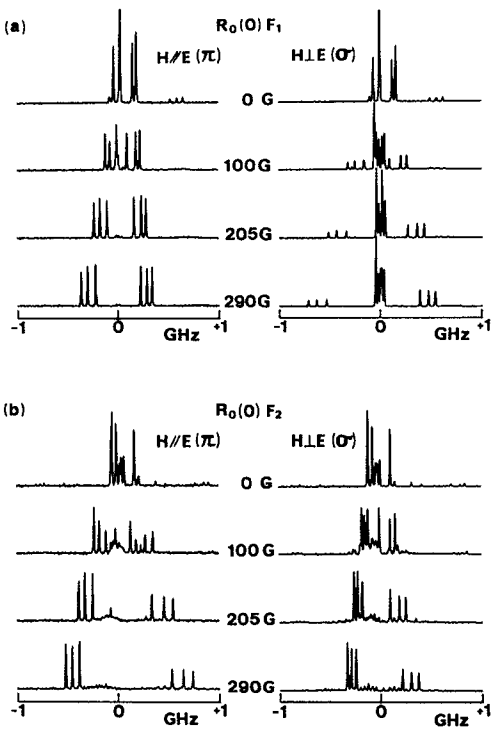

FIG. 2. Expanded spectra and the changes with the magnetic field of the $R_0(0)$ lines of the 593.3 nm band.

results of g-factor measurements in the weak magnetic field.[4,5]

We observed such large Zeeman splittings for the transitions to other $|K'=0,N'\rangle$ levels. It can be understood by the difference of the wave functions between the $^2A_1$ and $^2B_2$ states. In the $|K''=0,N''\neq 0\rangle$ level, there exist two spin sublevels, but the ZFS is very small in the $^2A_1$ state ($\gamma''=-0.00146\ \mathrm{cm}^{-1}$). Therefore, at about 300 G, the wave function in the $^2A_1$ state is already changed to $|^2A_1,K''=0,N''M_N\rangle|SM_S\rangle|IM_I\rangle$, while that in the $^2B_2$ state is represented by $|^2B_2,K'=0,N'SJM_J\rangle|IM_I\rangle$. Then, the Zeeman splitting becomes large even though the g value is about the same for both levels. However, the ZFS becomes large for the $K''\neq 0$ levels,[10] which leads small Zeeman splitting because the Zeeman shift of each magnetic sublevel is similar in both the $^2A_1$ and $^2B_2$ states.

We found the Zeeman pattern of the excitation spectrum strongly depended on the rotational and spin levels. The number of the split lines depended on N and the splitting on K, and the intensity distribution was different between the F_1 and F_2 levels, as seen in Fig. 1. Consequently, such Zeeman patterns of the high-resolution spectrum make easy to assign the rotational lines which are irregularly shifted by perturbations.

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