Laser magnetic resonance study of the v_2 bending of NO_2 using a CO_2 laser: Line positions and intensities

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ABSTRACT

The v_2 rovibrational bands ($010 \leftarrow 000$ and $020 \leftarrow 010$) of NO_2 were studied using CO_2 laser magnetic resonance (LMR). Thirty-six CO_2-laser lines were used to record approximately 200 Zeeman resonances in the 886–982 cm^{-1} range with perpendicular polarization (E⊥H). All resonances were assigned using molecular parameters from the literature. The intensities of the LMR spectra (both overlapping and not overlapping) were calculated, and the most intense spectra were assigned using the analysis. A new type of LMR signal, which was non-resonant, was observed and described.

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1. Introduction

Nitrogen dioxide ($^{14}N^{16}O_2(X^2A_1)$) is an important atmospheric molecule involved in the photochemistry of the stratosphere and in the pollution of the troposphere. Furthermore, nitrogen dioxide is one of the very few stable polyatomic free radicals; thus, this molecule is very attractive from a methodological point of view as a calibrant in laser magnetic resonance (LMR) studies. Thus, a defined concentration of nitrogen dioxide may be easily placed in a detection. The production of almost all other radicals requires a discharge-flow system or photolysis, therefore, determining their concentration is normally difficult. The absorption cross sections of the LMR lines of NO_2 can be calculated. Therefore, measuring LMR signal amplitudes provides information about the sensitivity of the LMR spectrometer. With these measurements, the concentrations of another radical R can also be determined by comparing the amplitudes of the LMR signals for NO_2 and R, assuming the same CO_2-laser line; the absorption cross section of R should also be known (such as for Cl, FO, and ND_2 [1]). Therefore, obtaining LMR spectra for NO_2 at the maximum number of CO_2-laser lines is very desirable.

The spectroscopy of NO_2 is well established. There have been numerous investigations of the line positions and intensities of the ground state and the v_2 band of NO_2 by using high-resolution techniques [2–16]. In the present study, we primarily used the data from the GEISA spectroscopic database [17].

Only one published LMR study, by Hakuta and Uehara [18], reports line positions measurements and v_2 band analysis. Hakuta and Uehara did not calculate the line intensities and only presented well-resolved spectra. Moreover, they used only one polarization (E∥H). Finally, only transitions with low N ($N \leqslant 17$, less than half of the rotational partition function) were analyzed.

The main objectives of the present study were to experimentally determine the LMR line positions in the perpendicular polarization, E⊥H; calculate the LMR line strengths; and to predict the strongest lines, which are normally unresolved. Such unresolved overlapping lines are normally useless for line position analysis, but these lines are often strong and very useful for application purposes. We have focused on E⊥H polarization because it is the Faraday LMR configuration.

2. Experimental details

Our intracavity LMR apparatus has been described in detail elsewhere [19–21]. The apparatus mainly consists of a tunable, single-mode, CO_2 laser, an absorption cell built in the laser cavity, a Ge–Hg photoresistor, a 30-cm electromagnet, field modulation coils, and a lock-in amplifier.

The absorption cell contains two Brewster-angle NaCl windows and was placed between the pole caps of the electromagnet. In all of our experiments, the electric vector of the laser radiation and the applied magnetic field were perpendicular to each other

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$(E \perp H)$. Therefore, the selection rule for electric dipole transitions was $\Delta M_J = \pm 1$.

The magnetic field was measured using an SH1–8 Holl-effect based detector, and the detector was calibrated using well-known LMR spectrum of Cl atoms [22–24]. Cl atom transitions are known with an accuracy of approximately 1 G [23]. Thus, the accuracy of our magnetic field measurements depended mainly on the uncertainty of the detector ($\sim$6 G). The maximum magnetic field was 5.4 kG.

The magnetic field was modulated at a resonance frequency of the CO_2-laser cavity (130 kHz), and the double modulation amplitude was varied in the range of 30–60 G. The modulation signal was also used to provide a reference signal to the lock-in amplifier.

The output radiation of the CO_2 laser (0.1–0.5 W) was coupled out from the zero-order reflection of the grating. The radiation was focused on the Ge–Hg photoresistor, which was cooled by solid N_2 ($\sim$53 K). The photoresistor signal was detected by the lock-in amplifier and sent to the Y pin of an XY recorder while the X axis was swept in synchrony with the magnetic field. The detection zone (limited by the modulation field length) was 12 cm long. The minimum detectable signal was determined by the laser noise.

The laser frequencies were determined using a monochromator; however, for safety reasons, absorption by C_2H_4/NH_3 mixtures was also used [25] to identify the laser lines. The CO_2-laser frequency was stabilized to the maximum of the gain profile using a piezoelectric translator on the laser output mirror.

The sample pressure was P_{NO_2} =5–15 Torr. From the equilibrium constant $k_P(T = 296K) = P_{NO_2}^2/P_{N_2O_4} = 0.123$ we know that the pressure of N_2O_4 was approximately 1 Torr. However, the N_2O_4 dimer is invisible in LMR because it is diamagnetic.

We searched for the LMR spectra of NO_2 in the P (34)–R (34) range of laser lines, which are 884–938 cm^{-1} and 931–987 cm^{-1}, for the 11-μm transitions of the $^{13}C^{16}O_2$- and $^{12}C^{16}O_2$-lasers, respectively. The ν_2-band center is much lower, near 750 cm^{-1}; therefore, the absorption typically involved highly rotationally excited molecules, thus leading to poor sensitivity.

3. Theory and analysis

We used the data from the GEISA-2009 database [17] as a starting point of our analysis. The database contains all of the necessary information (i.e., energy levels, transition frequencies, intensities of lines, and self-broadening coefficients), except for the behavior of the Zeeman sublevels. In the analysis, the spin-rotation energies $E(N_{K_a,K_c},J)$ were restored from the hyperfine structures as follows [11,12]

$$E(N_{K_a,K_c},J) = \sum_{F=J-1}^{J+1} \frac{2F+1}{3(2J+1)} E(N_{K_a,K_c},J,F). \quad (1)$$

Hereafter, we denote the energies of the rotational levels as $E(N_{K_a,K_c},J,F)$, the energies without hyperfine interactions as $E(N_{K_a,K_c},J)$, and the energies without both spin-rotation and hyperfine interactions as $E(N_{K_a,K_c})$.

After the analysis, we found that all of our observations could not be explained by this approach. Therefore, we developed our own program to calculate the rovibrational spectra of NO_2. The molecular parameters for the vibrational states (000), (010), and (020) were from Refs. [12,11,10], respectively. To calculate the intensities of the rotational lines, we used the approach of Devi et al. [6]. The matrix elements for the Herman–Wallis factors were taken from Flaud and Camy-Peyret [26].

The CO_2-laser wavenumbers were taken from Ref. [27].

3.1. Zeeman sublevels in the magnetic field

The following simple spin-rotation and Zeeman Hamiltonian was proposed by Hougen [28]:

$$H_{sr} + H_Z = \gamma(\mathbf{J}^2 - \mathbf{N}^2 - \mathbf{S}^2) + \mu_B g_s \mathbf{S} \cdot \mathbf{H}, \quad (2)$$

where $\mathbf{H}$ denotes the magnetic field, $\mathbf{N}$ and $\mathbf{S}$ are the rotational and spin momenta, respectively; $\mathbf{J} \equiv \mathbf{N} + \mathbf{S}$; g_s = 2.00232 is the spin gyromagnetic ratio, and μ_B = 0.046686 cm^{-1}/kG is the Bohr magneton. The first term in Eq. (2) accounts for the isotropic spin-rotational interaction. Because S = 1/2, the rotational states with fixed N are split into the F_1 and F_2 levels with $J = N + 1/2$ and $J = N - 1/2$, respectively.

In the present study, we used the following more complicated Hamiltonian:

$$H_{sr} + H_Z = \sum_{i=a,b,c} \epsilon_{ii}(N_i S_i + S_i N_i)/2 + g_{ii}(H_i S_i + S_i H_i)/2. \quad (3)$$

When $|M_J| < (N - 1/2)$, the Hamiltonian matrix for given N_{K_a,K_c} and M_J quantum numbers is block diagonalized into 2×2 submatrices, which have the following form:

$$\begin{pmatrix} E(N_{K_a,K_c}) - \frac{\gamma(M_J+1/2)}{2} - \frac{\mu_B H(g_1+\Delta g(1))}{2} & \left(\frac{\gamma}{2} + \mu_B M_J H g_{12}\right)\sqrt{(N+1/2)^2 - M_J^2} \\ \left(\frac{\gamma}{2} + \mu_B M_J H g_{12}\right)\sqrt{(N+1/2)^2 - M_J^2} & E(N_{K_a,K_c}) + \frac{\gamma(M_J-1/2)}{2} + \frac{\mu_B H(g_1+\Delta g(-1))}{2} \end{pmatrix}, \quad (4)$$

where the first line (column) corresponds to $M_S = -1/2$ and $M_N = -M_J + 1/2$, and the second line (column) corresponds to $M_S = 1/2$ and $M_N = M_J - 1/2$. The other parameters are as follows:

$$\Delta g(i) = 2(g_2 R_1(i) - g_3 R_2(i))/[(2N-1)(2N+3)], \quad (5a)$$

$$g_{12} = (g_2 R_3 + 3g_3/2)/[(2N-1)(2N+3)], \quad (5b)$$

$$R_1(i) = R_3 M_N^2 - K_a^2 + 1/4, \quad (5c)$$

$$R_2(i) = M_N[3M_N^2 - N(N+1)], \quad (5d)$$

$$R_3 = 3K_a^2/N(N+1) - 1, \quad (5e)$$

$$\gamma = \frac{K_a^2(\epsilon_{aa} - (\epsilon_{bb} + \epsilon_{cc})/2)}{N(N+1)} + \frac{\epsilon_{bb} + \epsilon_{cc}}{2} + \frac{(-1)^\alpha \delta_{1,K_a}(\epsilon_{bb} - \epsilon_{cc})}{4} \quad (5f)$$

$$g_1 = [g_{aa} + (g_{bb} + g_{cc})/2]/2, \quad (5g)$$

$$g_2 = g_{aa} - (g_{bb} + g_{cc})/2, \quad (5h)$$

$$g_3 = (-1)^\alpha \delta_{1,K_a}(g_{bb} - g_{cc})/2, \quad (5i)$$

where $M_N = M_J + i/2$ is assumed. When $M_J = (N + 1/2)$ or $M_J = -(N + 1/2)$, the matrix is replaced by 1×1 matrices containing either the lower right diagonal element or the upper left diagonal element from matrix (4), respectively.

All of these matrix elements are in the literature [18]. We have only changed the notation to show the inheritance between the two Hamiltonians. For Hamiltonian (2), the equalities $g_{12} = \Delta g(1) = \Delta g(-1) = 0$ and $g_1 = g_s$ are assumed. Eq. (5f), which gives the spin-rotational splitting, was not used in the present work, because the energies of the F_1 and F_2 levels were taken from the GEISA database. The γ parameters were calculated from the GEISA spin-rotational splittings using [28] $E(N_{K_a,K_c}, J = N + 1/2) - E(N_{K_a,K_c}, J = N - 1/2) = \gamma(N + 1/2)$.

In principle, the most detailed Zeeman Hamiltonian was proposed by Bowater et al. [29], in which the interactions of an external magnetic field with the unquenched orbital angular momentum and with the molecular rotational magnetic moment are involved (g_{ii} and g_{ii}^r tensors, respectively); the $\Delta N \neq 0$ interactions induced by the magnetic field should also be taken into account. We attempted to model the spectra using the g_{ii}^r parameters and the magnetic field-induced interactions with $\Delta N \neq 0$, but we found that doing so does not improve the agreement between the predictions and the experimental data. This finding is most likely because the g_{ii}^r parameters are too small relative to g_{ii} and