

USE OF MEASUREMENT DATA ON ABSORPTION LINE SHIFTS TO DETERMINE THE POLARIZABILITY OF NO₂ MOLECULE IN THE 001 STATE

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The magnitudes of half-width and shift of NO₂ absorption lines of ν_3 band induced by noble gases pressure have been measured using a diode-laser spectrometer with $3 \cdot 10^{-4} \text{ cm}^{-1}$ resolution. The magnitudes of mean polarizability of NO₂ molecule in 001 vibrational state and z-components of the polarizability tensor in 000 and 001 states were determined from the measured shift coefficients for NO₂ - Ar, NO₂ - Kr, and NO₂ - Xe mixtures. The data obtained were used in calculation of NO₂ absorption line half-widths. The calculation results well agree with the experimental data.

The findings of an investigation into the molecular collisional line broadening and lineshift are important in the analysis of intermolecular interaction potential, determination of collisional cross-sections of particles in a gas, and electrooptical constants of molecules in excited vibrational-rotational states. The data on broadening and shift coefficients for absorption lines of triatomic molecules with a constant dipole moment (H₂O, H₂S, SO₂, NO₂, etc.) in the IR and visible find their practicality owing to the development of spectroscopic methods for analysis of gas composition of the atmosphere.

The measurements of broadening and shift coefficients for molecular vibrational-rotational lines by noble gases are of particular interest. It is the simplest case for theoretical analysis. The atoms of noble gases have completed electron shells and have no constant electric moment in the ground electronic state. The energy required to excite atoms of a noble gas is greater than the mean thermal energy, so the noble gas atoms can be considered structureless. The experimental data on dependences of the halfwidths (γ) and shifts (δ) of the absorption lines on the atomic mass and polarizability of a noble gas can be used to verify various approximations used in the line contour theory.

The data on the dependence of δ/γ for H₂O absorption line (transition $7_{07}-8_{18}$ of ν_2 band) on the duration of a collision are given in Ref. 1. Analysis of the data suggests that nonadiabatic processes prevail in the case of collisions with light atoms (He, Ne) and the adiabatic ones in the case of H₂O-Xe collisions.

Analysis of the experimental data on H₂O absorption lineshifts in $\nu_1 + 3\nu_3$ band by pressure of noble gases, He, Ne, Ar, Kr, and Xe, has demonstrated

the modified Anderson-Tsao-Curnutte method, free of interruption procedure,^{2,3} to provide a good agreement between calculations and experiment. The calculations of γ and δ for SO₂ absorption lines in ν_1 and ν_3 bands broadened by pressure of Ar, Kr, and Xe gases, performed by that method, well agree with the experimental data obtained using the diode laser spectrometer of high resolution.⁴ It is also shown in Ref. 3, that the polarization interaction contributes mainly (about 90%) into the shift magnitude. The shift magnitude therewith depends on the absorber's polarizability in the ground and excited states. That fundamentally provides for a possibility of estimating the polarizability of a molecule in the excited vibrational state from the lineshift measurements.

The broadening and shift coefficient measurements made for a few vibrational-rotational lines of NO₂ in ν_3 band broadened by pressure of Ar, Kr, and Xe gases are analyzed in this paper. The empirical data on shifts of these lines are used to estimate the magnitude of the mean polarizability, unknown earlier, and the z-components of polarizability tensors in the ground and excited vibrational states.

EXPERIMENT

The halfwidths and shifts of NO₂ absorption lines were measured with a diode laser spectrometer, a detailed description of which may be found, for example, in Ref. 5. Spectral resolution of the spectrometer is $3 \cdot 10^{-4} \text{ cm}^{-1}$ which allows the measurement of the shift coefficient values as small as 10^{-3} cm^{-1} . To record the shape of weak absorption lines corresponding to large rotational quantum

numbers N , we used a Herriot multipass cell with the path length of 4.7 m and the volume of the gas under study of 180 cm³. Strong lines near the ν_3 band center were recorded using a singlepass cell of 30 cm length.

The measurements were conducted with commercially available gases NO₂ (99.8%), Ar (99.999%), Kr (99.99%), and Xe (99.998%).

The relative wavenumber calibration was carried out using confocal interferometer (FSR = 0.01 cm⁻¹). The well known line positions of NO₂ or H₂O absorption lines were used for absolute calibration. Because of high density of lines in NO₂ absorption spectrum, the procedure of fitting the measured contour to Voigt profile⁶ by the least squares method was used to determine the halfwidth and the shift of an individual line. The halfwidth and the shift values were measured for the following NO₂ absorption lines of ν_3 band: 34_{3,32} → 35_{3,33}; 35_{3,32} → 36_{3,33}; 36_{3,34} → 37_{3,35}; 37_{1,36} → 38_{1,37}.

Figure 1 presents an example of an absorption line contour 34_{3,32} → 35_{3,33} in the pure NO₂ and in the mixture NO₂-Xe as an illustration of the spectrometer capability to measure small line shifts by pressure $\approx 10^{-3}$ cm⁻¹.

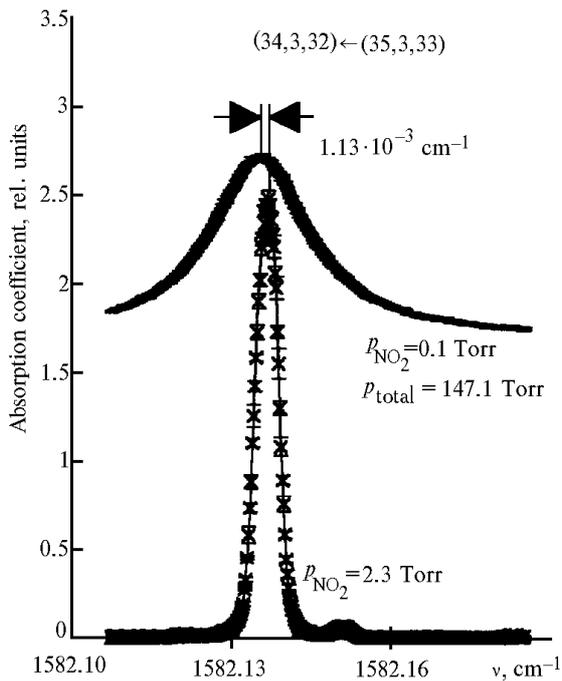


FIG. 1. Line shape of an NO₂ absorption line for pure NO₂ and NO₂ in a mixture with Xe.

The linear dependences of γ and δ on Xe pressure are shown in Figs. 2 and 3. The straight line slopes give the values of the broadening and shift coefficients. The measured values of these coefficients for all the above-listed lines and all noble gases are given in Table together with the rms errors varying from 0.1 to 0.5 mK (1 mK = 10⁻³ cm⁻¹).

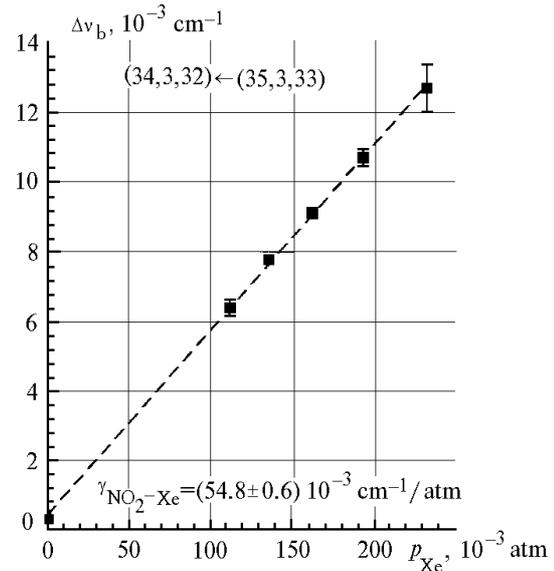


FIG. 2. Halfwidth of the NO₂ absorption line, Δv_b , on the pressure of a foreign gas, Xe.

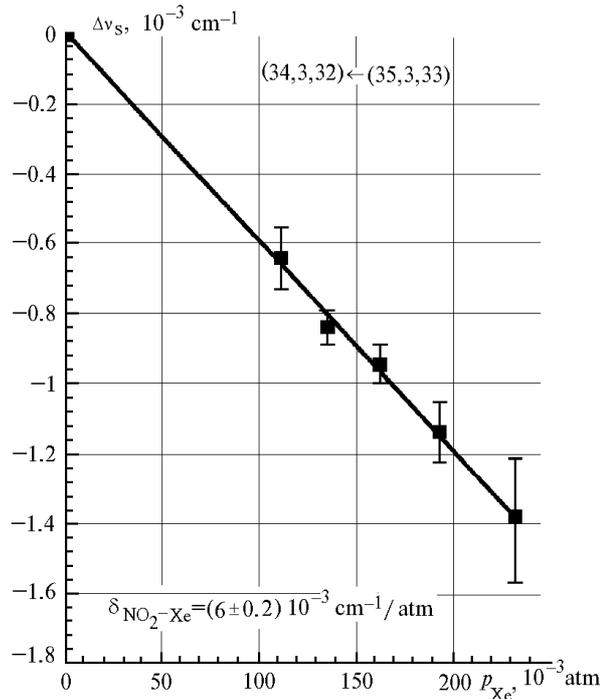


FIG. 3. Dependence of NO₂ absorption line center shift, Δv_s , on the pressure of a foreign gas, Xe.

The NO₂ molecule has incomplete electronic shell, so the collisions NO₂-NO₂ cause a dimerization due to the uncoupled electron. But, under conditions of the above-described experiment, the concentration of atoms of a noble gas is much higher than the concentration of NO₂ molecules, therefore we may neglect the contribution of NO₂-NO₂ collisions into the broadening and the shift of the NO₂ absorption lines.

TABLE I. The coefficient of line center shift of NO₂ absorption lines.

N'	k' _a	k' _c - N	k _a	k _c	ν _{if} , cm ⁻¹	Band ν ₃ , δ (mK·atm ⁻¹)			Band ν ₃ , γ (mK·atm ⁻¹)		
						Ar	Kr	Xe	Ar	Kr	Xe
34	3	32-35	3	33	1582.136	$\frac{-3.6 \pm 0.2}{-3.8}$	$\frac{-4.4 \pm 0.2}{-4.2}$	$\frac{-6.0 \pm 0.2}{-4.9}$	$\frac{52.3 \pm 0.6}{46.8}$	$\frac{49.5 \pm 0.5}{48.4}$	$\frac{54.8 \pm 0.6}{54.1}$
35	3	32-36	3	33	1581.082	$\frac{-3.3 \pm 0.2}{-3.9}$	$\frac{-4.6 \pm 0.2}{-4.5}$	$\frac{-6.2 \pm 0.3}{-5.4}$	$\frac{52.8 \pm 0.4}{46.7}$	$\frac{50.5 \pm 0.3}{48.2}$	$\frac{54.1 \pm 0.3}{53.9}$
36	3	34-37	3	35	1580.075	$\frac{-3.9 \pm 0.4}{-3.7}$	$\frac{-4.6 \pm 0.4}{-4.1}$	$\frac{-5.4 \pm 0.4}{-4.7}$	$\frac{50.1 \pm 2.7}{47.2}$	$\frac{46.8 \pm 2.3}{49.1}$	$\frac{54.1 \pm 2.1}{55.3}$
37	1	36-38	1	37	1580.476	$\frac{-3.2 \pm 0.3}{-3.8}$	$\frac{-5.3 \pm 0.1}{-4.2}$	$\frac{-6.9 \pm 0.1}{-4.8}$	$\frac{51.8 \pm 0.3}{47.0}$	$\frac{50.7 \pm 0.1}{48.4}$	$\frac{54.0 \pm 0.1}{54.0}$
						Mean deviation of the calculated γ value from the experimental one, %					
						9.5		4.11		1	

Comment: the numerator shows experimental values while the denominator is calculated value.

The measured values of the shift coefficients were used in determination of NO₂ polarizability α(001) in the vibrational state 001 and z-components α_{zz}(000) and α_{zz}(001) of the polarizability in the states 000 and 001. The axis z therewith was chosen perpendicular to the molecule plane.

The values α(001), α_{zz}(000), and α_{zz}(001) were determined by fitting procedure that implies minimization of the functional

$$\left\{ \sum_i^n |\delta_{\text{exp}}^i - \delta_{\text{calc}}^i(i)(\alpha(001), \alpha_{zz}(000), \alpha_{zz}(001))| \right\} / n \leq 0.001 \text{ cm}^{-1}. \quad (1)$$

The fitting parameter was taken equal to a doubled measurement error.

The fitting was performed separately for the cases of broadening by Ar, Kr, and Xe of four absorption lines. The mean value of the parameters sought, for example, $\bar{\alpha}(001)$, was determined as

$$\bar{\alpha}(001) = \frac{1}{3} \{ \alpha(001)_{\text{NO}_2\text{-Ar}} + \alpha(001)_{\text{NO}_2\text{-Kr}} + \alpha(001)_{\text{NO}_2\text{-Xe}} \}. \quad (2)$$

The fitting procedure is based on the "golden section" and the coordinate descent methods.⁷

The applicability of such approach to determination of H₂O molecule polarizability was earlier demonstrated in Ref. 8.

CALCULATION OF THE HALFWIDTH AND SHIFT OF NO₂ SPECTRAL LINES

The magnitudes of γ and δ are found using the expressions^{2,3}

$$\gamma = \frac{n}{c} \int_0^\infty F(v) v dv \int_0^\infty b db \times \{ 1 - \exp[-\text{Re } S(b)] \cos[\text{Im } S(b)] \}; \quad (3)$$

$$\delta = \frac{n}{c} \int_0^\infty F(v) v dv \int_0^\infty b db \times \{ \exp[-\text{Re } S(b)] \sin[\text{Im } S(b)] \}, \quad (4)$$

where n is the number concentration of the buffer gas atoms; c is the speed of light in vacuum; v is the speed of relative motion of the colliding molecules; F(v) is the Maxwell speed distribution function; b is the impact parameter.

The interruption function S(b) = S₁(b) + S₂(b) as an approximation of the dipole-polarization interaction is

$$S_1(b) = \left[-i \frac{3\pi}{8hv b^5} \right] [(d_i^2 - d_f^2) \alpha + \bar{\varepsilon} \alpha (\alpha_i - \alpha_f)]; \quad (5)$$

$$\text{Re } S_2(b) = \frac{21 \pi^2}{1280 (hv)^2 b^{10}} \left\{ \sum_i C_{20}(i2; i'2) \times \text{Re } g_1(k_{ii'}) + \sum_{f'} C_{20}(f2; f'2) \text{Re } g_1(k_{ff'}) - 2 WC_{20}(i2; i2) C_{20}(f2; f2) \right\}; \quad (6)$$

$$\text{Im } S_2(b) = \frac{21 \pi^2}{1280 (hv)^2 b^{10}} \left\{ \sum_{i'} C_{20}(i2; i'2) \times \text{Im } g_1(k_{ii'}) - \sum_{f'} C_{20}(f2; f'2) \text{Im } g_1(k_{ff'}) \right\}, \quad (7)$$

where d_i and d_f are the dipole moments; α_i and α_f are the polarizabilities of the absorbing molecule in the ground (i) and excited (f) vibrational states; α₂ is the polarizability of the buffer gas atom; $\bar{\varepsilon} = \varepsilon_1 \varepsilon_2 / (\varepsilon_1 + \varepsilon_2)$, where ε₁ and ε₂ are the ionization potentials of a molecule and an atom. The values C₂₀(i2, i'2) and C₂₀(f2, f'2) are the squares of the

reduced matrix elements determining the probability of transitions between rotational levels in the ground ($i \rightarrow i'$) and excited ($f \rightarrow f'$) vibrational states of the absorbing molecule. The function C_{20} is given in Ref. 7. Index 2 denotes quantum numbers of a noble gas molecule. The resonance functions $g_1(k_{ii'})$ and $g_1(k_{ff'})$, where $k_{ii'} = 2\pi cb\omega_{ii'}/v$ and $k_{ff'} = 2\pi cb\omega_{ff'}/v$ are the Massey's parameters, and depend on the frequencies of virtual rotational transitions $\omega_{ii'}$ and $\omega_{ff'}$, impact parameter b , and on the speed of relative motion of colliding particles v , $W = (j_i j_i' j_f j_f' / 12)$ is the Racah coefficient.

The functions $C_{20}(i2, i'2)$ depend both on the mean polarizability of absorbing molecule in the ground (α_i) and excited (α_f) vibrational states and on the corresponding z -components of the polarizability tensor α_i^{zz} and α_f^{zz} . The expressions for them may be found in Ref. 9. The characteristics of NO₂ molecule, needed in calculations, are taken from Ref. 10. The constant dipole moment of the NO₂ molecule in the ground vibrational state $d_i = 0.31D$ and the static polarizability $\alpha(000) = 3.02 \cdot 10^{-24} \text{ cm}^3$. The dipole moment value is known with $\approx 1\%$ error and the value of the static polarizability – with a 10% error. The NO₂ ionization potential ε_1 equals 9.78 eV. The values of the noble gases' polarizability and their potentials are the following:

$\varepsilon_{\text{He}} = 24.587 \text{ eV};$	$\alpha_{\text{He}} = 0.207 \cdot 10^{-24} \text{ cm}^3;$
$\varepsilon_{\text{Ne}} = 21.564 \text{ eV};$	$\alpha_{\text{Ne}} = 0.397 \cdot 10^{-24} \text{ cm}^3;$
$\varepsilon_{\text{Ar}} = 15.759 \text{ eV};$	$\alpha_{\text{Ar}} = 1.642 \cdot 10^{-24} \text{ cm}^3;$
$\varepsilon_{\text{Kr}} = 13.999 \text{ eV};$	$\alpha_{\text{Kr}} = 2.480 \cdot 10^{-24} \text{ cm}^3;$
$\varepsilon_{\text{Xe}} = 12.130 \text{ eV};$	$\alpha_{\text{Xe}} = 4.010 \cdot 10^{-24} \text{ cm}^3.$

The values of energy of NO₂ rotational levels in the ground and excited vibrational states as well as the corresponding transition frequencies ω_{ii} and ω_{ff} were calculated by formulas from Refs. 11 and 12 using the algorithm from Ref. 13. The initial, well-known, expressions for energy are rather cumbersome, so they are not presented here.

We estimate the value of NO₂ dipole moment in the excited vibrational state 001 to be equal to $0.317D$. It is 2% higher than the value of d_i in the ground state and typical for small molecules like, for example, SO₂ or H₂O^{14,15} at the quantum number change by 1.

RESULTS AND DISCUSSION

The mean value of the NO₂ polarizability in the 001 state determined by Eq. (2) turned out to be $(3.1 \pm 0.15) \cdot 10^{-24} \text{ cm}^3$, i.e. by 2.5% exceeding its value in the ground state. The obtained values of the polarizability tensor's z -components in the ground and excited states are: $\alpha_{zz}(000) \approx (2.1 \pm 0.2) \cdot 10^{-24} \text{ cm}^3$ and $\alpha_{zz}(001) \approx (2.15 \pm 0.2) \cdot 10^{-24} \text{ cm}^3$, i.e. less than the corresponding mean values, as in the case with the related molecules of asymmetric top type, SO₂, for example. In that case $\alpha(000) = 3.72 \cdot 10^{-24} \text{ cm}^3$ and $\alpha_{zz} = 2.7 \cdot 10^{-24} \text{ cm}^3$ (see Ref. 16). For $\alpha(000)$,

$\alpha_{zz}(000)$, $\alpha(001)$, and $\alpha_{zz}(001)$, the physically evident condition $\alpha(000)/\alpha_{zz}(000) \approx \alpha(001)/\alpha_{zz}(001) \approx 1.44$ is fulfilled. The obtained values of $\alpha(001)$, $\alpha_{zz}(001)$, and $\alpha_{zz}(000)$ were used in calculations of the broadening coefficients for five absorption lines of NO₂ in a mixture with Ar, Kr, and Xe. These results are given in Table I (the calculated values are in the denominator). Good agreement between the calculated and measured values of γ shows that the data on the NO₂ polarizability obtained are realistic. When calculating the broadening and shift coefficients, we didn't take into account a contribution from a constant quadrupole moment of NO₂ into its interaction with atoms of noble gases. This contribution into the calculated values (and the values $\alpha(001)$ and $\alpha_{zz}(001)$) depend on the difference between the values of NO₂ hyperpolarizability in the ground and excited vibrational states. At a difference $\leq 2\%$, the estimates obtained by formulas from Ref. 17 indicate the corrections to the shift coefficients to be insignificant because the shift is proportional to the difference between perturbations of the upper and lower levels.

In calculations of the halfwidth of a line, when an additional perturbation of levels is summed, the calculated value of γ may increase due to the contribution from NO₂ constant quadrupole moment. But, the exact estimation of this contribution is difficult because of the lack of data on the NO₂ hyperpolarizability. The experimental data on the broadening and shift of spectral lines of NO₂ vibration bands could also be used for simultaneous estimation of the hyperpolarizability and polarizability characteristics, but this problem is beyond the scope of this paper.

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