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Enhancement of Raman Scattering Intensity Due to an Internal-Field Factor

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Abstract—Enhancement of intensity of Raman scattering signals of gas-media components due to an internal-field factor induced by molecular environment is analyzed. Intensity of fundamental vibrational-rotational Raman band of nitrogen in mixtures with argon and methane at pressures of up to 50 atm is investigated. It is established that intensity of Raman signals of nitrogen at its fixed concentration in the mixtures varies within 4% depending on pressure and environment. A model describing this effect is proposed. Obtained data allow improving the accuracy of gas analysis based on Raman spectroscopy.

Keywords: Raman light scattering, signal intensity amplification, internal field, methane, nitrogen

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INTRODUCTION

Sensitivity of gas analyzers on the basis of Raman spectroscopy considerably improved in the past 10–20 years. As of today, detection limit means of such devices is below 1 ppm [1–3], which opens an opportunity of their application for controlling multicomponent gas media such as natural gas [4–7], exhaled air [8–10], air in the atmosphere [3, 11], etc. Most probably, sensitivity of Raman analyzers will become even higher in the near future due to improving characteristics of photodetectors and development of methods increasing intensity of Raman signals [2, 6, 10, 12–17]. However, a number of specific features that were ignored in the past due to low signal-to-noise ratio must be taken into account for extracting the most reliable values of concentration from the Raman spectra. Interrelation between Raman-signal intensity and concentration of molecules in one of them. Contrary to a widely spread opinion that the dependence between these quantities is linear, experimental results [18–20] indicate that this relation deviates from linear. This behavior is explained by the fact that electric field changes depending on density of the medium at the location of the studied molecule, which causes changes in intensity of Raman signals [21]. This effect is referred to as the internal-field factor and, according to [22], is a function of refractive index of the medium. This factor reveals itself most clearly in increase in effective scattering cross sections (the product of the scattering cross section and the internal-field factor) of molecules in a liquid relative to the gas phase [18]. According to [19, 20], this effect manifests itself also upon increase in pressure of the gas medium (without changes in the aggregate state), although, to a much lesses extent. Based on the available results, it is logical to assume that changes in molecular environment can also lead to variation of intensity of Raman signals per unit concentration of molecules. Currently, this problem is topical because the effect of changes in intensities when concentrations are determined by decomposition of Raman spectrum of a multicomponent mixture into spectra of individual components [7] can increase the error of measurements in the situation in which the reference spectra and the spectra of a mixture are obtained under different conditions (pressure and environment). In this regard, the present work aims at development and verification of a model that describes modification of intensities of Raman signals in gas mixtures.

THE THEORY

Intensity I_R of Raman signals of an individual vibrational-rotational band ν_j emitted from volume V into solid angle $\Delta\Omega$ for molecules of one kind can be presented in the form

$$I_R = I_L V \sigma_j \Delta\Omega \frac{P}{kTZ(P,T)} L(P) S(P), \qquad (1)$$

where I_L is the intensity of the excitation laser radiation, σ_j is the differential scattering cross section (for fixed observation angle of scattered radiation with respect to directions of polarization and propagation of the excitation radiation), k is the Boltzmann constant, T is temperature, P is pressure, $Z(P, T)$ is the gas compressibility factor, $L(P)$ is the internal field factor, and $S(P)$ is the coefficient describing variation of collection angle $\Delta\Omega$ with pressure P relative to collection angle at 1 atm (the instrument factor). For the sake of simplicity, henceforth, we will omit dependences on temperature and pressure in notations for Z, L, and S.

Let us analyze the internal field factor of a mixture L_{mix}. According to [22]

$$L_{\text{mix}} \approx \left[\frac{(n_{\text{mix}})^2+2}{3}\right]^4, \qquad (2)$$

where n_{mix} is the refractive index of the mixture at the laser-radiation frequency.

Using molecular refraction of a gas, this factor can be presented in the form [20]

$$L_{\text{mix}} \approx \left[1-\left(\frac{P_{\text{mix}}A^R_{\text{mix}}}{RTZ_{\text{mix}}}+\frac{P^2_{\text{mix}}B^R_{\text{mix}}}{R^2T^2Z^2_{\text{mix}}}\right)\right]^{-4}, \qquad (3)$$

where A^R_{mix} and B^R_{mix} are the first and the second virial coefficients of mixture refraction, respectively; P_{mix} and Z_{mix} are pressure and compressibility factor of the mixture, respectively. Coefficients A^R_{mix} and B^R_{mix} can be expressed in terms of compressibility factors of individual components of the mixture:

$$A^R_{\text{mix}} = \sum_{i=1}^{n} x_i A^R_i, \qquad (4)$$

$$B^R_{\text{mix}} = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B^R_{ij}, \qquad (5)$$

where n is the number of mixture components, and x_i is the fraction of molecules of the ith kind in the mixture. Note that $B^R_{ii} \equiv B^R_i$. If virial coefficients B^R_{ij} are unknown, they can be estimated using expression [23]

$$B^R_{ij} = \sqrt{B^R_i B^R_j}. \qquad (6)$$

Compressibility factor of the mixture Z_{mix} can be expressed in terms of compressibility factors of its individual components Z_i and mixture composition by the following equation:

$$Z_{\text{mix}} = 1-\left\{\sum_{i=1}^{n} x_i\sqrt{[1-Z_i]}\right\}^2. \qquad (7)$$

Compressibility factors Z_i, in turn, can be found by solving equation

$$Z_i^3 - Z_i^2 - \frac{PB(T)}{RT}Z_i - \frac{P^2C(T)}{R^2T^2} = 0, \qquad (8)$$

where $B(T)$ and $C(T)$ are the second and the third virial coefficients of the compressibility, respectively.

Table 1. Values of virial coefficients for nitrogen, argon, and methane at $T = 300$ K

Gas	B, cm^3/mol	C, cm^6/mol^2	A^R, cm^3/mol	B^R, cm^6/mol^2
N_2	−4.5 [24]	1500 [24]	4.4464 [25]	0.89 [25]
Ar	−15 [24]	1080 [24]	4.197 [25]	2 [25]
CH_4	−43 [24]	2400 [24]	6.576 [25]	6.08 [25]

EXPERIMENTAL

According to (1) and (2), intensity of Raman signals from the ith component can be increased due to internal-field factor induced by surrounding molecules. To verify this conclusion, we studied binary mixtures. The first one consisted of nitrogen (as the main gas) and argon (as the buffer gas). Nitrogen has only one fundamental band. Consequently, redistribution of intensities in its spectrum upon variation of conditions (pressure and temperature) is ruled out. Since argon is an atomic gas, it lacks the Raman spectrum. Hence, variation of intensity of signal from nitrogen when its concentration in a mixture with argon is fixed can be caused either by specifics of the used instrument or the internal-field factor. The second mixture consisted of nitrogen (as the main gas) and methane (as the buffer gas). Compared to argon, methane is characterized by a different compression factor and a different index of refraction (Table 1). Therefore, the internal-field factor for these two gases will be different at equivalent values of pressure.

An experimental setup described in [7, 20] was used for obtaining the Raman spectra. To minimize the influence of the instrument factor upon increase in pressure, we used two $f/4$-objectives with a focal distance of $f = 105$ mm instead of a pair of $f/1.8$-objectives with focal distance of $f = 50$ mm in the setup for collection of scattered light. At the first stage, we obtained the Raman spectrum of pure nitrogen at 1 atm. After that, we obtained spectra of N_2 (1 atm) + Ar (P) and N_2 (1 atm) + CH_4 (P) mixtures in which pressure P was varied from 4 to 49 atm in steps of 5 atm. The cycle of measurements was repeated 5 times to increase reliability of the experimental results. The purity of gases used in the experiments exceeded 99.99%. Mixtures were prepared in a preliminary mixing chamber ($V = 2000$ cm^3). After that, a measurement cell ($V = 10$ cm^3) was filled with a prepared gas mixture. Nitrogen pressure upon preparation of mixtures was controlled by means of a pressure gauge with an error of 0.02%. Hence, it can be stated that concentration of nitrogen molecules being analyzed was stable in all mixtures with this level of accuracy. Pressure of gas mixtures was controlled by a pressure gauge with an error of 0.05%. Laser power was controlled by means of a photodiode with an error of <0.1%. Each spectrum was recorded with an exposure

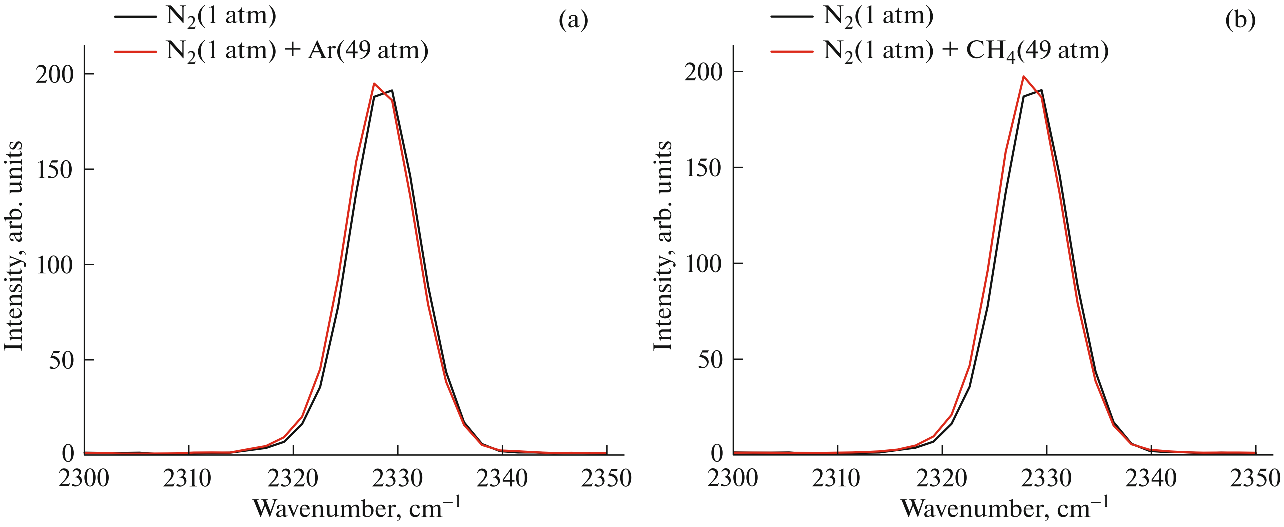

Fig. 1. Raman spectra of nitrogen in atmospheres of argon (a) and methane (b) in comparison to the spectrum of pure nitrogen.

time of 500 s. The temperatures of air in the laboratory and the gas cell was maintained at 300 ± 1 K.

RESULTS AND DISCUSSION

Specific feature of the Raman spectrometer used for the measurements was its negligibly low level of stray light and therefore low background in the spectra. For this reason, we did not use preliminary processing of N_2 + Ar spectra before determining intensities. At the same time, spectra of $N_2 + CH_4$ contained a background in the vicinity of the Raman band of nitrogen caused by scattering from intense lines of the methane pentad $2\nu_4$, $\nu_2 + \nu_4$, ν_1, ν_3, and $2\nu_2$. To take the background into account, spectrum of pure CH_4 obtained at pressure P was subtracted from each spectrum of N_2 (1 atm) + CH_4 (P). As a result of this operation, in fact, we obtained the spectrum of nitrogen the spectral characteristics of which were determined by methane environment.

The Raman spectra of nitrogen obtained in different environment are illustrated in Fig. 1. It can be seen that intensity of the spectrum somewhat increased in media with argon and methane. In order to get quantitative estimates, an integral intensity in the range from 2200 to 2500 cm^{-1} was determined for all recorded spectra of nitrogen. Raman spectra of nitrogen revealed a shift of up to 0.45 cm^{-1} and broadening of the Q-branch of up to 0.15 cm^{-1} caused by an increase in pressure. Note that, taking into account a relatively broad range in which intensities were integrated, these spectral changes did not affect obtained values.

Changes in refractive index caused by changes in the gas pressure in the cell lead to changes in effective focal distance of the objective used for scattered radiation collection. As a result, collection solid angle $\Delta\Omega$ appearing in (1) also changes, which causes changes in the detected intensity. A special procedure was used to estimate this instrument factor. Since the latter depends on refractive index, we calculated an increase in the effective focal distance of the objective used for collection of scattered light for different values of n_{mix}. The required values of refractive index were calculated using Eq. (2) in which L_{mix} was calculated using equations (3)–(8). Maximum increase in the focal distance was found to be 0.22 mm for the N_2 (1 atm) + CH_4 (49 atm) mixture. After that, we obtained a set of Raman spectra of pure nitrogen at fixed pressure of 1 atm wherein the discussed objective was installed at different distances in the range from 0 to 0.2 mm from the optical axis of the laser radiation propagating inside the cell. Alignment of the experimental setup and all parameters of registration of spectra remained unchanged. Approximation of obtained data yielded the dependence of variation of intensity on refractive index of the gas in the cell. Taking into account calculated values of n_{mix} (Table 2), we obtained the values of the instrument factor for each mixture.

Averaged experimental values of the integral intensity of nitrogen band for various values of pressure and different environment normalized to integral intensity at 1 atm are presented in Fig. 2. The confidence intervals represent standard deviation obtained from 5 measurements. It can be seen that intensity increased with buffer-gas pressure in both mixtures. In the process, the enhancement was higher in the methane environment, reaching 4% in the N_2 (1 atm) + CH_4 (49 atm) mixture. Taking into account the confidence intervals, we note that the experimental data were close to theoretical, which proves the validity of the model presented above.

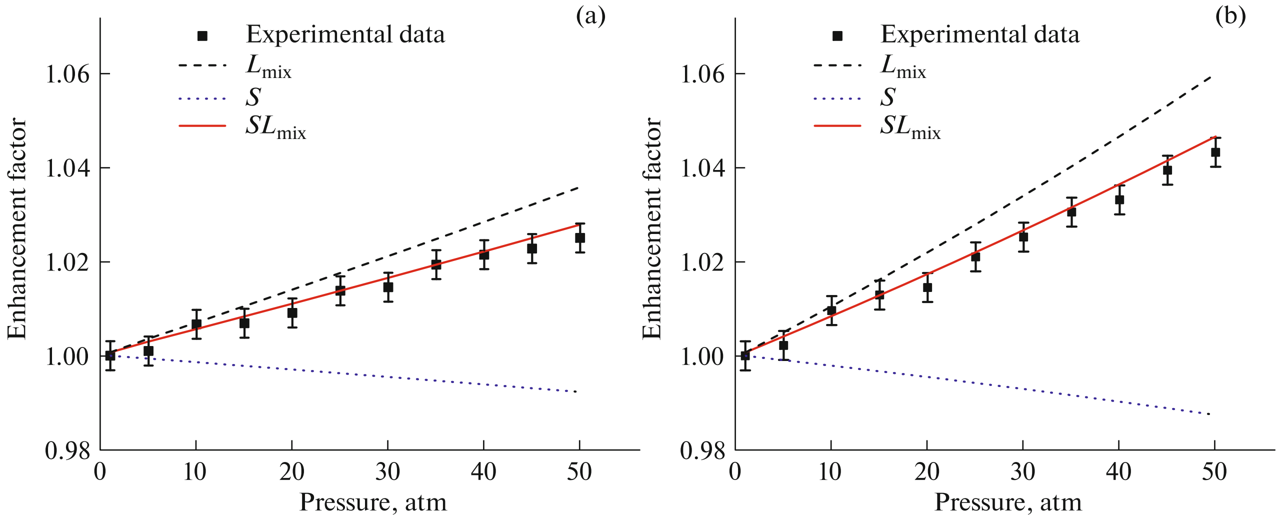

Fig. 2. Values of internal-field factor L_{mix}, instrument factor S, their product SL_{mix}, along with experimental values of the integral-intensity enhancement factor of the Raman signal of nitrogen as a function of pressure of N_2 + Ar (a) and $N_2 + CH_4$ (b) gas mixtures.

Let us analyze the influence of the discussed effect on the accuracy of Raman analysis. Method of contour fitting [7] represents the most efficient method of calculation of concentrations in multicomponent mixtures (such as, e.g., natural gas) in which spectra of different components substantially overlap with each other. However, implementation of this method for in situ analysis of natural gas (NG) requires specific preparation of reference spectra. This is because, in order to minimize errors, all reference spectra must have spectral characteristics (the half-width and the shift) equivalent to the conditions in which the NG sample spectrum was obtained [26, 27]. Pressure of NG in gas pipelines, in turn, can reach 100 atm, while spectra of pure hydrocarbons C2+ cannot be obtained in a gaseous state under such pressure at room temperature. For example, maximum pressure of propane at $T = 300$ K is ~6 atm, that of butanes is ~2 atm, pressure of pentanes is ~0.5 atm, etc. For this reason, binary mixtures with a buffer gas can be used instead of pure hydrocarbons when preparing the reference spectra. It is advantageous using an atomic gas (e.g., argon) as a buffer gas because it lacks a Raman spectrum. Spectrum of any hydrocarbon characterized by half-width and shift of the lines close to those observed in an NG sample can be obtained by varying the buffer gas pressure in such a mixture. Taking into account the effect of internal field, intensity of Raman signals in the mixtures will be higher relative to spectra of pure components. According to Fig. 2, this increase will be as high as 2% when using argon at $P = 50$ atm. This will result in an increase in the error of determining concentration of a given hydrocarbon by the same amount. Since developers of Raman gas analyzers aim at replacing gas chromatographs, a 2% increase in error is considerable, because an uncertainty of the method of gas chromatography lies within 6% [28]. In this regard, in order to increase the accuracy of the measurements, the effect of internal field has to be taken into consideration.

Table 2. Values of refractive index, compressibility factor, and internal-field factor for N_2(1 atm) + CH_4(P) and N_2(1 atm) + Ar(P) gas mixtures

	N_2(1 atm) + CH_4(P)			N_2(1 atm) + Ar(P)		
P, atm	n_{mix}	Z_{mix}	L_{mix}	n_{mix}	Z_{mix}	L_{mix}
0	1.00027	0.9998	1.0007	1.00027	0.9998	1.0007
4	1.00188	0.9952	1.0050	1.00136	0.9982	1.0035
9	1.00393	0.9870	1.0106	1.00272	0.9955	1.0069
14	1.00602	0.9786	1.0162	1.00408	0.9927	1.0104
19	1.00814	0.9702	1.0219	1.00544	0.9899	1.0139
24	1.01031	0.9618	1.0279	1.0068	0.9872	1.0175
29	1.01251	0.9535	1.034	1.00817	0.9846	1.0211
34	1.01476	0.9453	1.0402	1.00953	0.9820	1.0247
39	1.01704	0.9372	1.0466	1.0109	0.9795	1.0284
44	1.01936	0.9293	1.0532	1.01226	0.9771	1.0321
49	1.02172	0.9215	1.0599	1.01362	0.9748	1.0358

CONCLUSIONS

Presented data demonstrate that intensity of the Raman signal of an analyzed gas can increase due to internal field created by the surrounding molecules. On the one hand, this effect can be realized by adding a considerable volume of any atomic gas (due to the lack of Raman spectrum) to the gas under investigation. At high pressures, this can cause an increase in the Raman intensity by several tens of percent. On the other hand, in order to improve the accuracy of the measurements, the described effects must be taken into account in the procedure of determining concentrations from the Raman spectra.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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