DETERMINATION OF THE COLLISIONAL LINEWIDTH AND RELATIVE INTENSITY IN THE METHOD OF BROADBAND INTRACAVITY LASER SPECTROSCOPY

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Simple method for processing of time-integrated broadband spectra of intracavity laser absorption is developed that allows one to obtain the values of collisional widths and relative intensities of isolated homogeneously broadened lines based on two parameters of a spectrogram measured as well as on the width of the instrumental function of a classical spectrometer used for recording intracavity absorption spectra.

Up to date a great number of absorption line centers of different gases have been measured using the method of intracavity laser spectroscopy (ICLS)[1,2] that allowed a number of inverse problems of molecular spectroscopy aimed at estimation of intramolecular force field constants to be solved.[3,4] At the same time, ICL spectra also contain very important information about collisional widths and intensity of lines, which, as a rule, is not used, because in order to retrieve it one should use either a very complicated procedure for spectrum processing[5] or an extremely sophisticated experimental technique allowing the recording of a series of instantaneous spectra during a pulse.[6,7] The procedure already existing for processing of time-integrated spectra[1,11] has been developed to handle relatively narrow spectra of a ruby laser generation. Its width is only several times greater than the width of an absorption line under study. That is why this procedure is rather complicated too and involves different numerical methods.

This paper proposes a procedure which needs no numerical methods. This procedure is developed to process the time-integral ICL spectra, whose width is much greater than the width of an isolated Lorentzian molecular absorption line. The procedure is based on simple algebraic equations describing the shape of dips in selective absorption in the lasing spectra recorded using a classical spectrometer. Using this procedure, by measuring relative dip depths and widths, one can find the relative intensity and homogeneous (collisional) widths of absorption lines, free of the influence of the spectrometer instrumental function.

General principles of this procedure are the following:

1. If the interaction of laser radiation with a selectively absorbing medium (molecular gas at a pressure near or above the atmospheric one) is assumed linear, then the lasing power in the region of selective absorption related to the power at the same frequency ω without the selective absorption is usually described by the modified Bouguer law:

$$G(\omega, t) \propto \exp[-k(\omega)\, ctl/L], \qquad (1)$$

where $k(\omega)$ is the absorption coefficient of the gas under study, c is the light speed, t is current time from the beginning of lasing, l and L are the optical lengths of the absorbing cell and the cavity, respectively. The theoretical calculation[8–10] of $G(\omega, t)$ yields the equation, which differs from Eq. (1) by only the factor $\sqrt{t}$ at the exponent, that is of small significance from the viewpoint of determination of the spectral dependence since it enters into the exponent only. The experiments[6,7] showed the dependence (1) to be suitable for quantitative description of ICL spectra recorded.

2. The time-integrated spectrum $J(\omega)$ is proportional to the integral of $G(\omega, t)$ multiplied by the factor giving the shape of lasing pulse. In the limiting cases of short and long laser pulses (pulse duration, τ_p, is much shorter or longer than the time $\tau_0 \equiv L/[ck(\omega)l]$ characterizing the absorption), as a result of integration with the use of rectangular shape of laser pulses, the spectrum $J(\omega)$ can be presented as

$$J_1(\omega) \propto G(\omega, t_{\text{eff}}), \quad \tau_p \ll \tau_0, \qquad (2a)$$

$$J_2(\omega) \propto [1 - G(\omega, t_{\text{eff}})]/k(\omega), \quad \tau_p \gg \tau_0. \qquad (2b)$$

Numerical calculations show[11] that the assumptions (2) well suit the quantitative processing of spectra when using nonrectangular symmetric pulses with the error $\leq 6\%$. For the continuous-wave lasing, the value τ_p is replaced by the average duration of spontaneously arising wave trains of lasing in the vicinity of an absorption line.[9] The value t_{eff} in Eq. (2) is the effective duration of lasing, being of the same order of magnitude as τ_p, which is naturally to be

used as the fitting parameter when making a comparison with the experiment.

3. A dip against the background of a broad lasing spectrum corresponds to an isolated absorption line of a medium inside the cavity (see Fig. 1). Without loss of generality, the continuous lasing spectrum in the vicinity of an isolated absorption line can be considered a constant value, and its amplitude can be taken as unity. The maximum dip value I, its halfwidth at halfmaximum δ, and the depth P_2 at the distance 2δ from the center are used, in the procedure developed, for determining true parameters of the absorption coefficient $k(\omega)$, and the directly measured parameters in such an approach are I and δ.
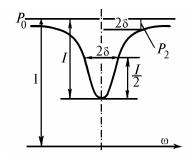

FIG. 1. Dip in the ICL spectrum.

4. The shape of the absorption coefficient $k(\omega)$ and the instrumental function of a classical spectrometer $f_{ins}(\omega)$ are believed Lorentzian:

$$k(\omega) = \frac{1}{\pi\gamma}\frac{S}{1 + (\omega/\gamma)^2}, \; f_{ins}(\omega) = \frac{1}{\pi\gamma_{ins}}\frac{S}{1 + (\omega/\gamma_{ins})^2}, \quad (3)$$

where S is the line strength; γ is the homogeneous (collisional) line halfwidth at halfmaximum; γ_{ins} is the spectrometer instrumental function halfwidth at halfmaximum.

5. It is seen from Eqs. (1)−(3) that the value of the ratio

$$\sigma \equiv Sct_{eff}\, l/(\pi\gamma L) \quad (4)$$

establishes the distinct line between the cases (2a) and (2b), namely, at $\sigma < 1$ dips in the spectrum will be not very deep $(0 < I < 0.5)$, while at $\sigma > 1$ they will be deep $(0.5 < I < 1)$. That is why it is worthwhile turning from the two limiting cases (2a) and (2b) to the general formula that approximates the dip shape $P(\omega)$ without a marked increase in the error of representation throughout the whole range of the dip depth:

$$P(\omega) = (1 - I)[1 - J_1(\omega)] + I\,[1 - J_2(\omega)]. \quad (5)$$

6. Spectrum recording with a classical spectrometer leads to convolution of expressions (2a) and (2b) with the instrumental function $f_{ins}(\omega)$, Eq. (3),

$$\tilde{J}_1(\omega) = \frac{1}{\pi}\int\limits_{-\infty}^{\infty}\frac{dx}{(x - \omega)^2 + 1}\exp\left[-\frac{\sigma}{1 + (x/\gamma)^2}\right],$$

$$\tau_p \ll \tau_0, \quad (6a)$$

$$\tilde{J}_2(\omega) = \frac{1}{\pi\sigma}\int\limits_{-\infty}^{\infty}dx\,\frac{1 + (x/\gamma)^2}{(x - \omega)^2 + 1}\left\{1 - \exp\left[-\frac{\sigma}{1 + (x/\gamma)^2}\right]\right\},$$

$$\tau_p \gg \tau_0. \quad (6b)$$

In Eqs. (6) and below all values having the dimensionality of frequency are measured in the units of the spectrometer instrumental function halfwidth $\gamma_{ins} \equiv 1$. As a consequence of an obvious relation, following from Eqs. (6a) and (6b):

$$\tilde{J}_2(\omega, \sigma) = \frac{1}{\sigma}\int\limits_{0}^{\sigma}\tilde{J}_1(\omega, \sigma_1)\,d\sigma_1\,, \quad (7)$$

further it is sufficient to calculate only $\tilde{J}_1(\omega, \sigma)$.

Expanding the exponent in the integrand of Eq. (6) into a series and integrating it term-by-term using the theory of residues, the following expressions for the dip shape $P_1(\omega) = 1 - \tilde{J}_1(\omega)$ can be derived

$$P_1(\omega) = -\sum_{n=1}^{\infty}\frac{(-\sigma)^n}{n!}\sum_{m=1}^{n}(g\zeta)^m\sum_{l=0}^{\min(m,n-m)}\frac{1}{4^{n-m}}\frac{m+l}{m}\times$$
$$\times\binom{m}{l}\binom{2n - m - l - 1}{n - 1}(-g)^l\,, \quad (8)$$

$$P_1(\omega) = -\sum_{m=1}^{\infty}\frac{(g\sigma)^m}{m!}\,_2F_2\left(\frac{m}{2}, \frac{m+1}{2}; m, m+1; -\sigma\right)\times$$
$$\times\sum_{l=\left[\frac{m+1}{2}\right]}^{m}\frac{1}{4^{m-l}}\frac{m}{l}\binom{l}{m-l}(-\zeta)^l\,; \quad (9)$$

$$g \equiv \gamma/(1 + \gamma), \;\; \zeta \equiv 1/\{1 + [\omega/(1 + \gamma)]^2\}, \;\; m \le n, \;\; n \ge 1,$$

where $\binom{r}{s}$ are the binomial coefficients; $[p/q]$ is the integer part of a fraction; $_2F_2$ is a hypergeometric function. When deriving Eqs. (8) and (9), we have used the following expression, obtained by the method of mathematical induction:

$$\sum_{l=0}^{\min(m,n-m)}\frac{(-1)^l}{2^{2n-m-l-1}}\binom{2n - m - l - 1}{n - 1}\times$$

$$\times\sum_{k=0}^{\left[\frac{m-l}{2}\right]}\binom{m+l}{2l+2k}\binom{l+k}{k} = \delta_{m,n}\,. \quad (10)$$

For the area S_1 of a dip P_1 from Eq. (8) we obtain the equation

$$S_1 = \int\limits_{-\infty}^{\infty} d\omega \, P_1(\omega) = \pi\gamma\sigma\,\Phi\left(\frac{1}{2},\, 2;\, -\sigma\right), \qquad (11)$$

where $\Phi(\cdots)$ is the degenerate hypergeometric function.

The expressions for the dip $P_2(\omega) = 1 - \tilde{J}_2(\omega)$ analogous to Eqs. (7) and (8) can be readily obtained from the latter ones by applying the expression (7).

Let us write the first seven terms of the series (8):

$$\frac{P_1(\omega)}{\sigma Z} = 1 - \frac{1}{2}\,\sigma\left(\frac{1}{2} - \frac{1}{2}\,g + Z\right) +$$

$$+ \frac{1}{6}\,\sigma^2\left[\frac{3}{8}\,(1-g)(1+2Z) + Z^2\right] -$$

$$- \frac{1}{24}\,\sigma^3\left\{(1-g)\left[\frac{5}{16} + \frac{1}{8}\,(5-g)Z + Z^2\right] + Z^3\right\} +$$

$$+ \frac{1}{120}\,\sigma^4\left\{(1-g)\left[\frac{35}{128} + \frac{5}{64}\,(7-2g)Z + \right.\right.$$

$$\left.\left. + \frac{5}{16}\,(3-g)Z^2 + \frac{5}{4}\,Z^3\right] + Z^4\right\} -$$

$$- \frac{1}{720}\,\sigma^5\left\{(1-g)\left[\frac{63}{256} + \frac{21}{128}\,(3-g)Z + \right.\right.$$

$$\left. + \frac{1}{32}\,(28-14g+g^2)Z^2 + \frac{3}{16}\,(7-3g)Z^3 + \frac{3}{2}\,Z^4\right] + Z^5\Big\} +$$

$$+ \frac{1}{5040}\,\sigma^6\left\{(1-g)\left[\frac{321}{1024} + \frac{21}{512}\,(11-4g)Z + \right.\right.$$

$$+ \frac{7}{128}\,(15-9g+g^2)Z^2 + \frac{7}{64}\,(6-g)(2-g)Z^3 +$$

$$\left. + \frac{7}{8}\,(2-g)Z^4 + \frac{7}{4}\,Z^5\right] + Z^6\Big\} ; \qquad (12)$$

$$Z \equiv g\zeta.$$

The residual term in Eq. (12) is of the order of $\sigma^7/40\,320$. Assuming it equal, for example, to 0.02, for the maximum value of σ at which the expansion (12) is accurate to 2% we find $\sigma = 2.6$, that allows us to describe the dips $P_1(\omega)$ with the depth $I \le 0.7$.

Having substituted Eq.(8) and analogous expression for $P_2(\omega)$ into Eq. (5), we obtain the representation of the equation for a dip $P(\omega)$ as a series

$$P(\omega) = (1 - I)\,P_1(\omega) + I P_2(\omega) =$$

$$= \sigma Z \sum_{n=1}^{\infty} \frac{(-\sigma)^n}{n!}\left(1 + \frac{n}{n+1}\,I\right)\pi_n(g, Z) ;$$

$$\pi_n(g, Z) = \sum_{m=1}^{n} Z^{m-1} \sum_{l=0}^{\min(m,n-m)} b_{nml}(-g)^l ; \qquad (13)$$

$$b_{nml} = \frac{1}{4^{n-m}}\,\frac{m+l}{m}\binom{m}{l}\binom{2n-m-l-1}{n-1} .$$

7. The maximal depth I of the dip and its halfwidth δ are determined from the relations

$$I \equiv P(\omega = 0), \quad P(\omega = \delta) = \frac{1}{2}\,I, \qquad (14)$$

where $P(\omega)$ is given by Eq. (13). Having restricted our consideration by the first six terms of the power series in σ in Eq. (13), we present the sought parameters σ, Eq. (4), and g, Eq. (9), which are directly related to the relative line intensity and its halfwidth γ, as six-order polynomials in I. Unknown coefficients of these polynomials can be found by substituting the latter ones into Eqs. (14) and (13) with following expanding the parameters $\zeta(\delta, \gamma)$ into analogous polynomials, grouping the like terms, and sequentially solving the set of two linear algebraic equations at different powers of I. The final result of these transformations is

$$\sigma = \frac{\delta I}{\delta - 1}\left[1 + \frac{2\delta - 1}{2(\delta - 1)}\,I + \frac{96\delta^2 - 89\delta + 23}{96(\delta - 1)^2}\,I^2 + \right.$$

$$+ \frac{384\delta^3 - 493\delta^2 + 234\delta}{384(\delta - 1)^3}\,I^3 +$$

$$\left. + \frac{92160\delta^4 - 145011\delta^3 + 93511\delta^2 - 31439\delta + 4879}{92160(\delta - 1)^4}\,I^4\right]; \qquad (15)$$

$$g = \frac{\gamma}{1+\gamma} = \frac{1}{\delta}\left[\delta - 1 - \frac{1}{4}\,I - \frac{23\delta - 17}{96(\delta - 1)}\,I^2 - \right.$$

$$- \frac{87\delta^2 - 120\delta + 44}{384(\delta - 1)^2}\,I^3 -$$

$$- \frac{19576\delta^3 - 37483\delta^2 + 25505\delta - 6119}{92160(\delta - 1)^3}\,I^4 -$$

$$\left. - \frac{72959\delta^4 - 116592\delta^3 + 25718\delta^2 + 39576\delta - 18055}{368640(\delta - 1)^4}\,I^5\right]. \qquad (16)$$

With the help of the definition $P_2 \equiv P(\omega = 2\delta)$ and Eqs. (13), (15), and (16), we find with the same accuracy:

$$P_2 = \frac{1}{5}\,I + \frac{7}{25}\,I^2 + \frac{420\delta^2 - 479\delta + 135}{3000(\delta - 1)^2}\,I^3 -$$

$$- \frac{3216\delta^3 - 9651\delta^2 + 6886\delta - 3353}{240000(\delta - 1)^3}\,I^4 . \qquad (17)$$

8. The order of processing spectrograms like the one presented in Fig. 1 is as follows:

(i) with the orientation to the far wings of the dip $P(\omega)$, the zero level of the dip $P_0 \equiv P(\omega \to \infty)$ is approximately determined, which is, at the same time, the level of maximum power $J_{\max}$ (lasing power without a selective absorption);

(ii) the spectrum is normalized to the value of $J_{\max}$;

(iii) the dip center is found, and the values I and δ are measured;

(iiii) the value $P_2 \times J_{\max}$ is calculated and plotted above the curve $P(\omega)$ at a distance 2δ from the dip center, and the refined position of the zero level P_0 is thus determined;

(iiiii) steps (ii) − (iiii) are repeated, and the values I and δ obtained are compared with the previous ones; if their relative difference is below a preset level of error (∼ 1−3%), then the substitution of the last thus obtained values I and δ into Eqs. (15) and (16) gives the sought values of σ and γ.

As a rule, to reach the level of accuracy about a few per cent, one−two iterations following the above−described scheme of processing are sufficient. It is easy to generalize this order of processing also for the case, when the dip background (the value J_{max}) linearly depends on the frequency (wavelength) of radiation.

9. In the above procedure for processing ICL spectra, the halfwidth γ_{ins} of the classical spectrometer instrumental function was assumed known (and taken to be unit). A convenient way for its determination may be the previous measurements of dip widths, corresponding to the absorption lines under study and recorded at a low gas pressure, when the inhomogeneous broadening takes place, i.e., the line profile is Doppler one. The point is that under room temperature the Doppler line widths $k\overline{v}$, where k is the wave number and $\overline{v}$ is the most probable speed, in the visible and near infrared regions are of the value from 0.03 ($\lambda = 0.35$ μm) to 0.006 cm^{-1} ($\lambda = 2$ μm). At the same time, typical values of halfwidth γ_{ins} are from several hundredth to several tenth of reciprocal centimeter, that can be several times greater than the Doppler widths. Thus, the value γ_{ins} can be estimated with a sufficient certainty. The scheme to find it is the same as the above one to find γ, only with the substitution of the Doppler line profile

$$k(\omega) = S / (\sqrt{\pi}\, k\, \overline{v}) \exp[-(\omega / k\overline{v})^2] \qquad (18)$$

for the Lorentzian one.

In the experiments performed specially to find γ_{ins}, by varying the gas pressure in the measuring cell, every time it is possible to restrict the consideration to small dip depths, i. e. the case $\tau_p \ll \tau_0$. In this case the expression for the dip shape has the form

$$P_1(\omega) = 1 - \frac{\gamma_{ins}}{\pi} \int_{-\infty}^{\infty} \frac{dx}{(x - \omega)^2 + \gamma_{ins}^2} \exp(-\sigma e^{-x^2}); \qquad (19)$$

$$\sigma = S c t_{eff}\, l / (\sqrt{\pi}\, k\, \overline{v} L) .$$

Expanding the exponent in Eq. (19) into a series and integrating it term-by-term, we obtain

$$P_1(\omega, \gamma_{ins}, \sigma) = - \sum_{n=1}^{\infty} \frac{(-\sigma)^n}{n!} \operatorname{Re} w\, [\sqrt{n}\, (w + i\gamma_{ins})] ;$$

$$w(z) = e^{-z^2}\left[1 + \frac{2i}{\sqrt{\pi}} \int_0^z e^{t^2}\, dt \right], \qquad (20)$$

where $w(z)$ is the probability integral of the complex argument, and $\operatorname{Re} w(z)$ is the Voigt profile.

The calculated dependence of γ_{ins} on the halfwidth δ of the profile (20) in the interval of the dip depth $I \leq 0.2-0.3$ and halfwidths $\delta \geq 1.5\, k\overline{v}$ can be well approximated by the following equation

$$\gamma_{ins} = \sqrt{\delta^{2.01} - 0.638} - 0.234 , \qquad (21)$$

where the values of γ_{ins} and δ are expressed in terms of $k\overline{v}$.

The procedure developed was applied to processing of experiment[12] on measuring the collisional widths and relative intensities of ICL absorption lines of water vapor in atmospheric air in the range 1.12−1.16 μm with the laser on F_2^-: LiF colors centers.

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