EMPIRICAL RELATIONS FOR CALCULATING THE OF HALFWIDTHS ATMOSPHERIC GASES SPECTRAL LINES

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The experimentally measured line half–widths were approximated by power polynomials over rotational quantum numbers. The polynomial coefficients for several atmospheric and foreign gases were determined using the least–squares method. The empirical relations are used as a version when compiling databases of spectral line parameters of the atmospheric and foreign gases.

We give account of the method for calculating the spectral line half–widths of atmospheric and foreign gases which is used as a version in compilation of databases of spectral line parameters of the atmospheric and foreign gases in the informational system of high resolution spectroscopy.[1]

The half–widths of gas compounds determined by a collisional effect are included into a database. They are usually calculated by the formula

$$\gamma_{x-\mathrm{air}} = 0.79\gamma_{x-N_2} + 0.21\gamma_{x-O_2} . \quad (1)$$

Normally, the line characteristic in question is a result of complex processes of intermolecular interactions, and a rigourous account of all the collisional effects leads to the development of algorithms which require a long processing time even for ES–1066 computers.

TABLE I. Coefficients of the empirical polinomial (1) for calculating half–widths of spectral lines of diatomic molecule (X is a compound, Y is a broadening gas, and γ is measured in $\mathrm{cm^{-1}\cdot atm^{-1}}$*).*

X–Y	a_0	a_1	a_2	a_3
$CO–N_2$	8.0195E–2	–3.1725E–3	1.5623E–4	–3.5836E–6
$CO–O_2$	7.4406E–2	–4.3546E–3	2.5452E–4	–5.3859E–6
CO–air	7.9159E–2	–4.0478E–3	2.4107E–4	–5.0578E–6
HF–air	1.2608E–1	2.7546E–3	1.6256E–3	1.9724E–6
$N_2O–N_2$	9.6340E–2	–1.4406E–3	2.8143E–5	–1.7428E–7
$N_2O–O_2$	8.6087E–2	–1.7102E–3	3.9542E–5	–3.3325E–7
$H^{35}Cl–N_2$	9.6610E–2	–2.8485E–3	–1.7594E–3	1.2240E–4
$H^{35}Cl$–air	8.9611E–2	–4.5899E–3	–1.1770E–3	8,8654E–5
CO_2–air	–1.1567E–1	1.7212E–2	–4.8627E–4	4.2599E–6

At the same time a smooth behavior of the line half–widths as a function of rotational quantum number enables one to describe it by empirical polynomials over the rotational quantum numbers. The use of such polynomials reduces the time of count by a factor of ten for O_3 and H_2O molecules that can essentially simplify engineering techniques for computing the transmission functions of gaseous media.

Attempts to approximate the line half–widths of diatomic and linear molecules by polynomials have been undertaken elsewhere.[2,12]

In this short communication we discuss the use of the polynomial to describe the half–width of diatomic and linear molecules

$$\gamma = \sum_{i=1} a_i J^i . \quad (2)$$

TABLE II. Coefficients of the empirical polynomial (2) for calculating half–widths of spectral lines of asymmetric–top molecule (H_2O, O_3*).*

i	a_i	b_i
	H_2O+air	
1	8.02931420378E–02	5.96878496366E–02
2	–2.23265376653E–02	–1.45933468655E–02
3	2.87550341412E–03	1.28676695819E–03
4	–1.86934312545E–04	–3.88585560027E–05
5	6.71461180136E–03	4.20180398279E–03
6	–6.67835081027E–03	2.17787647005E–03
7	4.5302368115E–03	–8.04798061814E–04
8	–9.72747802740E–04	6.34952740478E–05
	O_3+air	
1	1.69734630137E–02	1.35273908408E–01
2	–1.52844886551E–03	–2.22751585875E–01
3	6.06027218136E–05	1.33390899524E–01
4	–1.09036336167E–06	–3.21930124512E–02
5	7.25714815172E–09	2.67909372603E–03

In this polinomial the argument is the rotational quantum numbers of the lower state of the transition, in contrast to Refs. 2 and 12 where the polynomial argument is the number m which equals to J for P–branch, to zero for Q–branch, and $J + 1$ for the R–branch.

For triatomic asymmetric molecules we propose the formula

$$\gamma = \sum_{i=1} a_i J^i + \sum_{\kappa} b_k \Delta\tau^k , \quad (3)$$

where J is the rotational quantum number of the lower state of the transition resulting in a spectral line and $\Delta\tau = \tau' - \tau''$ is the difference between pseudoquantum numbers of the transition ($\tau = K_A - K_C$).

A minimization program has been written for calculating polinomial coefficients based on empirical data and the values of these coefficients are given in Tables I and II. The statistical processing mainly involved data on line half–widths measured in air as a foreign gas. When such data were unavailable we used experimentally measured half–width of lines broadened by nitrogen and oxygen and a relevant combination calculated by formula (1).

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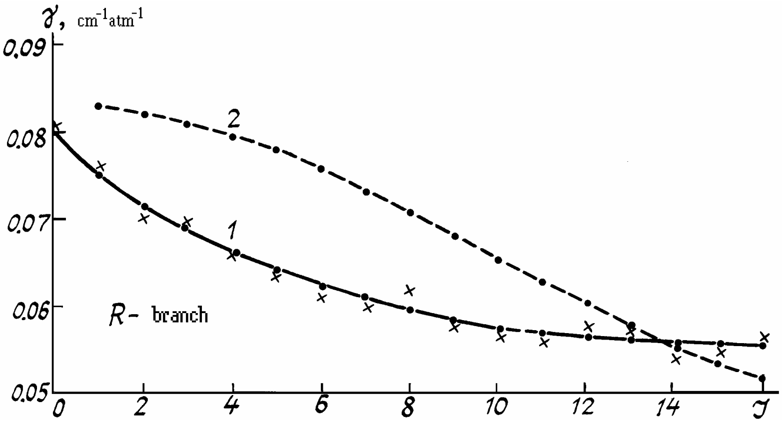

FIG. 1. Calculational data on the half–widths of CO *spectral lines in air obtained using the polynomial (1) (curve 1) compared to experiment (crosses), and curve 2 shows the calculations made by formula (3).*

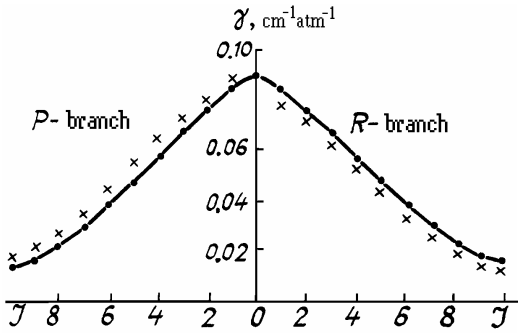

FIG. 2. Half–widths of the HCl *spectral lines broadened by air. Dots connected by solid lines present calculational data obtained using the polinomial representation and crosses are the experimental data from Ref. 4.*

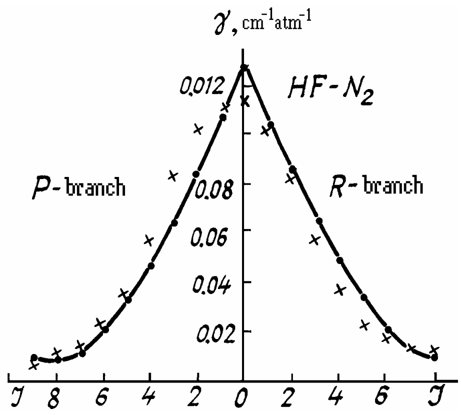

FIG. 3. Half–widths of the HF *spectral lines broadened by nitrogen molecules. Dots connected by solid lines present calculational data obtained using the polinomial representation and crosses show the experimental data from Ref. 4.*

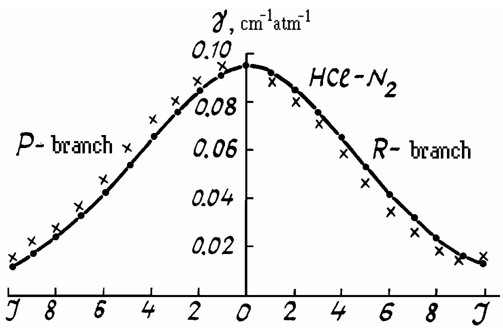

FIG. 4. Half–widths of the HCl *spectral lines broadened by nitrogen molecules. Dots connected by solid lines present calculational data obtained using the polinomial representation, crosses show the experimental data from Ref. 4.*

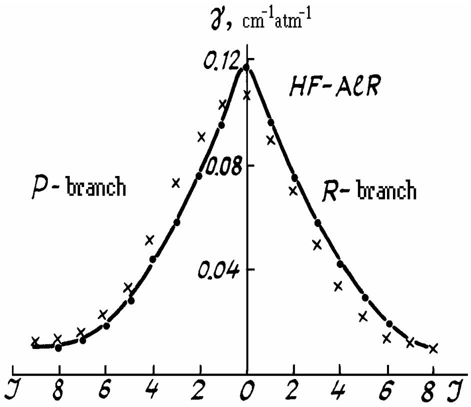

FIG. 5. Half–widths of the HF *spectral lines broadened by air. Dots connected by solid line present calculational data obtained using the polinomial representation, crosses show the experimental data from Ref. 4.*

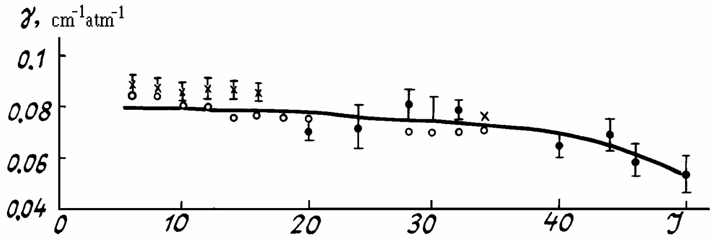

FIG. 6. Half–widths of the CO_2 *spectral lines. Solid line presents calculational data, circles show the experimental data from Ref. 6, crosses – from Ref. 7, and vertical bars show the experimental data from Ref. 5.*

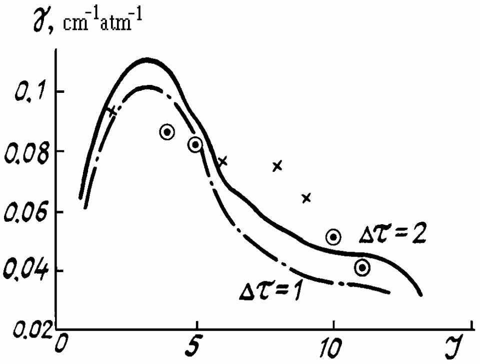

FIG. 7. Comparison of the calculated (solid line) values of the H_2O *line half–widths with experiment (encirled dots – Ref. 10 and crosses – Ref. 8).*

For a CO molecule there are three polinomials in Table I since for this molecule experimental data available are most comprehensive that allows one the calculational to estimate error of line half–widths in the case of air. Shown in Fig. 1 are the half–widths calculated based on the three polynomials for three broadening gases CO–N_2 CO–O_2 and CO–air. As can be seen from the figure, relation (1) gives an error of 20% at middle J values. Unfortunately, it is too difficult to explain unambiquosly such a discrepancy. Certain contribution can come from selfbroadening which has been neglected. Moreover, there may exist an effect of additional components of air. Figure 1 confirms the fact that the highest accuracy in determining the polynomial constants is provided for by processing of the experimental data on the air–broadened half–widths. Therefore we determine the polynomial for the combination CO_2–air. Moreover, the data for the pairs CO_2–N_2 and CO_2–O_2 are available from Ref. 12.

Figures 2–7 and Table III show the interpolation capability of the polynomials. Encircled dots in Fig. 7 present data on water vapor spectral line half–width not used in the fitting procedure. On the other hand, for the O_3 molecule in Fig. 8 are depicted the experimental data on the spectral half–widths used in the inverse problem and the curve calculated using thusly determined coefficients of the polinomial. The accuracy of reconstructing the experimental data from Ref. 9 is, on the average, 10 percent, though for some spectral lines it is poorer. However, the comparison of half–widths of the ozone spectral lines broadened by air as calculated using formula (3) with the experimental data[14] has shown the largest discrepancy to be about 15%.

TABLE III. Analysis of predictable capability of polynomial (1) for calculating the half–widths.

X–Y	δ_{av}	δ_{max}	δ_{min}
CO–N_2	1	6	0.08
CO–air	1	4	0.4
HF–air	2	10	1
N_2O–O_2	1	5	0.4
HCl–N_2	2.6	21	0.7
HCl–air	2.4	18	0.2

We have analyzed the available experimental data on the line half–widths in air based on Ref. 15.[15] For many data the situation was similar to that presented in Tables III and IV. Thus the proposed polynomials can be used in engineering techniques for calculating the optical transmittance.

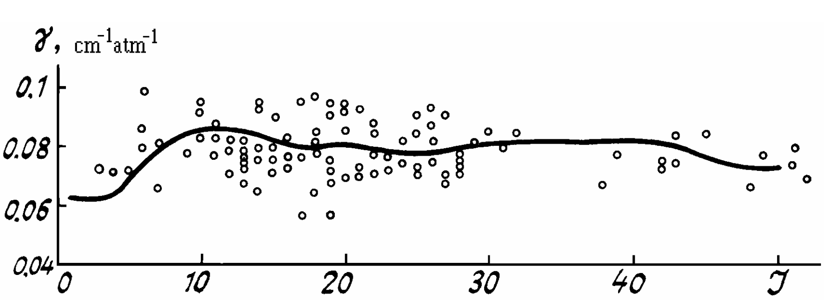

FIG. 8. Comparison of the calculated (solid line) values of the O_3 *line half–widths with experiment (circles – Ref. 9).*

TABLE IV. Comparison between the values of half–widths for O_3 calculated by formula (3) and those obtained in the independent experiment.[14]

Identification of transition	J'	K'_A	K'_C	J''	K''_A	K''_C	γ_{exp}	γ_{calc}	δ, %
	50	4	47	49	4	46	0.0743	0.072	3
ν_1	43	3	40	42	3	39	0.0800	0.079	1
	28	7	21	27	8	20	0.0826	0.079	4
	8	2	6	9	3	7	0.0717	0.066	8
	24	1	23	23	4	20	0.0788	0.077	2
	43	9	35	42	10	32	0.0825	0.078	6
ν_3	33	3	31	34	2	32	0.0841	0.082	3
	35	4	32	34	5	29	0.0688	0.081	18
	42	5	37	41	6	36	0.0695	0.080	15
	18	2	16	17	3	15	0.0828	0.081	2
	34	4	30	33	5	29	0.0744	0.082	10

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