Pressure Effects of Foreign Gases on the 535.0 nm Fluorescence Line of Thallium *

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Z. Naturforsch. **40 a,** 800 – 809 (1985); received April 4, 1985

Results of a series of experiments on pressure effects caused by various foreign gases on the 535.0 nm Tl fluorescence line emitted due to the photodissociation of TlI-molecules are summarized and some aspects of the Doppler and pressure broadening of this line are discussed. The impact broadening- and shift-cross sections are determined for two sets of mean relative velocities $\bar{v}$ of the emitter-perturber pair. An attempt is made to analyse the cross-sections for different perturbers by investigating their dependence on the quantity $(\alpha/\bar{v})^{2/5}$, where α is the polarizability of the perturber.

1. Introduction

In a series of experiments in this laboratory [1 – 10] the collision broadening and shift of the green fluorescence thallium line 535.0 nm ($7\,^2S_{1/2} - 6\,^2P_{3/2}$) perturbed by various foreign gases have been studied at densities low enough ($\leqq 4 \cdot 10^{18}$ cm^{-3}) for the impact approximation to be valid. The main goal of these studies was to provide information about interactions between thallium atoms in the $7\,^2S_{1/2}$ and $6\,^2P_{3/2}$ states and various perturbing particles such as noble gas atoms [4, 5], simple non-polar diatomic molecules H_2 [1, 2], D_2 [3], N_2 [6], O_2 [7] as well as the non-polar polyatomic molecules CO_2 [8] and SF_6 [9]. Recently, the collision broadening and shift studies on the 535.0 nm Tl line have been extended [10] by use of CO with its permanent electric dipole moment. Particular attention was paid to the analysis of the shape and shift of the line in order to obtain reliable values of the broadening and shift parameters. Line profile and shift measurements were performed by means of a photoelectric pressure-scanned Fabry-Perot interferometer and detailed analysis gave the shift of the line as well as the half-widths of both the Lorentzian and Gaussian components of the measured profile as functions of the gas density. To avoid the disturbing effects due to the ions and electrons giving rise to Stark effect in case of spectral lines emitted from discharge sources we have excited the atomic fluorescence of thallium at 535.0 nm by photodissociation of thallium iodide vapour due to irradiation with ultraviolet light from a radio-frequency electrodeless mercury vapour discharge lamp (henceforth called the 535 line for brevity). This technique was found to be very efficient and permitted measurements over a wide density range.

In the case of atomic fluorescence resulting from the photodissociation of the parent molecule, apart from the usual Doppler broadening caused by the thermal motion additional Doppler broadening may arise due to the additional kinetic energy of the photodissociation products *(recoil effect)*. Since the distribution of recoil velocities of fragment atoms is not Maxwellian, the resulting Doppler profile is not, in general, Gaussian. A numerical analysis performed in our laboratory has shown, however, that in spite of the above restriction the resultant Doppler profile of the 535 line may be in a good approximation described by a Gaussian profile but with the half-width significantly greater than the usual Doppler half-width corresponding to the cell temperature. This result enables one to analyse the profiles in terms of a Voigt profile as was done in Refs. [1 – 10].

For all foreign gases used in our experiments we found a linear variation of both the Lorentzian half-width γ_L and the shift Δ of the 535 line with the perturber density N, which is the typical behaviour in the impact regime. Based on these linear dependences the values $\beta = \gamma_L / N$ of the broadening and $\delta = \Delta / N$ of the shift coefficients were determined. The quantitative interpretation of these coefficients

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* This work was carried out under the Research Project M.R.I.5.

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in the framework of the impact theory [11–14] requires the knowledge of parameters describing the interaction between the thallium atom and the perturbing particles. Such an interpretation was given in Refs. [4] and [5] for the broadening and shift of the 535 line by noble gases assuming the Lennard-Jones model potential function. On the other hand, in the case of broadening and shift by molecular gases only a qualitative interpretation was given because of the lack of potential parameters.

The purpose of the present paper is threefold. Firstly, we discuss some aspects of the Doppler broadening of the 535 line. Secondly, results of our measurements of β and δ are summarized and presented in a uniform way in terms of corresponding so-called "impact" cross-sections σ_b and σ_s for the broadening and shift of the line, respectively, which seem to be more convenient quantities in theoretical analysis than the coefficients β and δ themselves. Thirdly, an attempt is made to analyse the cross-sections σ_b and σ_s for the 535 line perturbed by different foreign gases by investigating their dependence on the quantity, $(\alpha/\bar{v})^{2/5}$, where α is the polarizability of the perturbing particle and $\bar{v}$ is the mean relative velocity of the emitter-perturber pair.

2. Impact analysis

It is well known that in the impact approximation the profile of the pressure broadened and shifted spectral line is Lorentzian (cf. [11–13]) with the half-width γ_L and shift Δ proportional to the perturbing gas density N. The collision (or pressure) broadening and shift coefficients β and δ, respectively, can be written in the form

$$\beta = \frac{\gamma_L}{N} = \frac{2\,\overline{v\,\sigma_b}}{2\pi c} \tag{1}$$

and

$$\delta = \frac{\Delta}{N} = \pm\frac{\overline{v\,\sigma_s}}{2\pi c}, \tag{2}$$

where the quantities $\overline{v\,\sigma_b}$ and $\overline{v\,\sigma_s}$ can generally be written as

$$\overline{v\,\sigma_b} = \int_0^\infty f(v)\,v\,\sigma_b(v)\,dv \tag{3}$$

and

$$\overline{v\,\sigma_s} = \int_0^\infty f(v)\,v\,\sigma_s(v)\,dv\,. \tag{4}$$

Here $\sigma_b(v)$ and $\sigma_s(v)$ are the effective cross-sections for the broadening and shift, respectively, for a fixed value of the relative velocity v, and $f(v)$ is the distribution function of the relative velocities v. In (2) the sign "+" corresponds to blue shift and "−" to red shift.

In most papers on pressure effects on spectral lines one neglects the distribution of relative velocities assuming that

$$f(v) = \delta(v - \bar{v}), \tag{5}$$

where $\bar{v}$ is the mean relative velocity. In such an approximation (3) and (4) become

$$\overline{v\,\sigma_b} = \bar{v}\,\sigma_b(\bar{v}) \tag{6}$$

and

$$\overline{v\,\sigma_s} = \bar{v}\,\sigma_s(\bar{v})\,. \tag{7}$$

Numerical tests of the accuracy of this approximation have recently been done by Spielfiedel and Roueff [14] in the case of a Maxwellian velocity distribution for sodium resonance lines perturbed by He. They have shown that at room temperatures the discrepancy between the results obtained from the approximations given by (6), (7) and those obtained from (3), (4) using velocity averaging are of the order of 5%. On the other hand, however, their calculations seem to indicate that at very low temperatures averaging over a Maxwellian velocity distribution is necessary.

Since the accurate potential curves describing the interaction energy $V(R)$ between the emitting Tl-atom and the perturbing particle situated at the distance R from it are not known, we use here the Lennard-Jones potential

$$V(R) = \hbar\,(C_{12}\,R^{-12} - C_6\,R^{-6}), \tag{8}$$

where the parameters C_6 and C_{12} depend on the states of the emitting atom and the perturber. Following Unsöld [15], the C_6 parameter can be computed from the formula

$$C_6 = \frac{e^2}{\hbar}\langle r^2\rangle\,\alpha, \tag{9}$$

where e is the elementary charge and α the polarizability of the perturber. Here $\langle r^2\rangle$ is the expectation value of r^2 for a given state of the emitting atom.

Using this type of interaction potential and the impact treatment of Hindmarsh et al. [16], the broadening and shift cross-sections $\sigma_b(\bar{v})$ and $\sigma_s(\bar{v})$

may be expressed in the form

$$\sigma_\mathrm{b}(\bar v) = 13.42\left[\frac{e^2}{\hbar}(\langle r^2\rangle_\mathrm{u} - \langle r^2\rangle_\mathrm{l})\right]^{2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} B(\xi) \quad (10)$$

and

$$\sigma_\mathrm{s}(\bar v) = 6.709\left[\frac{e^2}{\hbar}(\langle r^2\rangle_\mathrm{u} - \langle r^2\rangle_\mathrm{l})\right]^{2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} |S(\xi)|, \quad (11)$$

where the subscripts u and l refer to the upper and lower state of the emitting atom, respectively. In (10) and (11), $B(\xi)$ and $S(\xi)$ are defined by the integrals

$$B(\xi) = \int_0^\infty x \sin^2[\tfrac{1}{2}(\xi x^{-11} - x^{-5})]\,\mathrm{d}x \quad (12)$$

and

$$S(\xi) = \int_0^\infty x \sin(\xi x^{-11} - x^{-5})\,\mathrm{d}x, \quad (13)$$

where the parameter ξ is given by

$$\xi = 0.536\left[\frac{e^2}{\hbar}(\langle r^2\rangle_\mathrm{u} - \langle r^2\rangle_\mathrm{l})\right]^{-11/5}\left(\frac{\bar v}{\alpha}\right)^{6/5}\frac{\Delta C_{12}}{\alpha}. \quad (14)$$

Here $\Delta C_{12} = C_{12}^{(\mathrm{u})} - C_{12}^{(\mathrm{l})}$.

The interaction of the perturber with the thallium atom in the initial state $7\,^2\mathrm{S}_{1/2}$ can be described by a single potential curve. In the final Tl-state ($6\,^2\mathrm{P}_{3/2}$) there are two potential curves corresponding to two values of the projection of atomic angular momentum on the internuclear axis. Nevertheless we assume here also for the final states a single potential curve, so that in this approximation we neglect the non-adiabatic effects in the $6\,^2\mathrm{P}_{3/2}$ Tl-state. Such an approach is well justified for the Van der Waals interaction only (cf. [17]), and therefore it may be responsible for the deviations of the experimental data from those computed from the adiabatic impact theory.

Other deviations may be connected with the use of the Lennard-Jones potential.

In the present work we computed $\langle r^2\rangle_\mathrm{u}$ and $\langle r^2\rangle_\mathrm{l}$ using the Coulomb approximation [15]

$$\langle r^2\rangle = \tfrac{1}{2}a_0^2(n^*)^2[5(n^*)^2 + 1 - 3l(l+1)], \quad (15)$$

where a_0 is the Bohr radius, n^* the effective quantum number and l the orbital quantum number. For thallium the values of n^* as given by Kuhn [18] are 2.195 for the state $7\,^2\mathrm{S}_{1/2}$ and 1.627 for $6\,^2\mathrm{P}_{3/2}$. Substituting these values into (15) and (10)−(14) we obtain the following expressions for the broadening and shift cross-sections of the 535 line:

$$\sigma_\mathrm{b}(\bar v) = 3.32\times10^{-2}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} B(\xi) \quad (16)$$

and

$$\sigma_\mathrm{s}(\bar v) = 1.66\times10^{-2}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{v}\right)^{2/5} |S(\xi)|. \quad (17)$$

If the repulsion part of the potential is neglected ($\Delta C_{12} = 0$, $\xi = 0$), the broadening and shift integrals in (12) and (13) reduce to constant quantities: $B(0) = 0.301$ and $S(0) = -0.438$. Then (16) and (17) become

$$\sigma_\mathrm{b}(\bar v) = 9.98\times10^{-3}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} \quad (18)$$

and

$$\sigma_\mathrm{s}(\bar v) = 7.26\times10^{-3}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5}. \quad (19)$$

These expression can also be obtained directly from the Lindholm-Foley expressions (cf. [13]) for the collision broadening β and shift δ coefficients:

$$\beta = 2.65\,\mathrm{g}^{-2/5}\,\mathrm{cm}^{-9/5}\,\mathrm{s}^{7/5}\,|\Delta C_6|^{2/5}\,\bar v^{3/5} \quad (20)$$

and

$$\delta = -0.963\,\mathrm{g}^{-2/5}\,\mathrm{cm}^{-9/5}\,\mathrm{s}^{7/5}\,|\Delta C_6|^{2/5}\,\bar v^{3/5}. \quad (21)$$

We should note that according to (18)−(21) for the Van der Waals potential the impact theory predicts a constant ratio of the cross-sections:

$$\frac{\sigma_\mathrm{s}(\bar v)}{\sigma_\mathrm{b}(\bar v)} = 2\frac{\Delta}{\gamma_\mathrm{L}} = 0.727. \quad (22)$$

The equations (18)−(21), which refer to pure Van der Waals interaction, can easily be generalized by replacing the assumption (5) by the assumption that the components of the relative velocity $\bar v$ have a Gaussian normal distribution. In this case (18) and (19) would have to be replaced by

$$\frac{\overline{v\sigma_\mathrm{b}}}{\bar v} = 0.9775\times9.98\times10^{-3}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} \quad (18\,\mathrm{a})$$

and

$$\frac{\overline{v\sigma_\mathrm{s}}}{\bar v} = 0.9775\times7.26\times10^{-3}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar v}\right)^{2/5} \quad (19\,\mathrm{a})$$

since

$$\int_0^\infty\left(\frac{v}{\bar v}\right)^{3/5} f(v)\,\mathrm{d}v = \frac{2^{2/5}}{\pi^{1/5}}\,\Gamma\left(\frac{9}{5}\right) = 0.9775.$$

3. Doppler Broadening

The profile measurements on the 535 line reported in [1–10] were performed using a pressure-scanned Fabry-Perot interferometer (spacer 1.204 cm, free spectral range $0.415\ \mathrm{cm}^{-1}$) with a photoelectric detector as described in the papers by Bielski et al. [19, 20]. Details of our numerical analysis of the 535 line are described in [1] (cf. also [4]).

For all densities of the perturbing gas we have found that the non-instrumental component of the measured shape of the 535 line can be fitted well to a Voigt profile, i.e. a convolution of Lorentzian and Gaussian profiles. Thus it seems that the Doppler shape of the 535 line is given by a Gaussian distribution. As was shown by Zare and Herschbach [21], in general the Doppler shape of fluorescence lines emitted by a fragment atom excited due to photodissociation of a parent molecule may differ significantly from a Gaussian profile. However, in the case of excitation by unpolarized light as in our experiments the Zare-Herschbach theory predicts Doppler line profiles which resemble very much the Gaussian profiles.

The usual Gaussian half-width $\gamma_\mathrm{d}^{(\mathrm{th})}$ resulting from the Doppler broadening due to thermal motion with the Maxwellian distribution of velocities is given by [15]

$$\gamma_\mathrm{d}^{(\mathrm{th})} = 2\frac{\nu_0}{c}\sqrt{\frac{2kT}{M}\ln 2}\,, \tag{23}$$

where ν_0 is the unperturbed frequency and M the mass of the emitting atom. For the 535 line at the temperature 733 K, at which all measurements in [1–10] were performed, (23) yields

$$\gamma_\mathrm{d}^{(\mathrm{th})} = 0.025\ \mathrm{cm}^{-1}.$$

Following Zare and Herschbach [21], the Doppler half-width γ_d' of a line emitted due to the photodissociation in case the recoil velocity is small in comparison to the thermal velocity of the parent molecule, can be estimated from a formula identical to (23) but with M being the mass of the parent molecule rather than the emitting atom. For TlI at $T = 733$ K we get then $\gamma_\mathrm{d}' = 0.020\ \mathrm{cm}^{-1}$.

According to Zare and Herschbach the recoil velocity can in principle be calculated from the final relative kinetic energy of the Tl* and I atoms, corresponding to a particular value of the rotational angular momentum of the excited (TlI)* molecule (cf. (27) in [21]). Because of the lack of data on potential curves for the excited (TlI)* molecule, such a calculation cannot be performed at present. Let us note, however, that in our experiments the recoil velocities may be greater than the thermal velocity of the TlI molecule. This conclusion can be drawn from a rough estimation based on the comparison of the energy of the exciting photon to the threshold energy 6.04 eV, which is the sum of the TlI ground state dissociation energy (2.76 eV) recommended by Huber and Herzberg [22] and the $\mathrm{Tl}(7\,^2S_{1/2})$ excitation energy.

In all our experiments we have found that for all perturbing gases the values of the resultant half-width γ_g of the Gaussian component of the measured profile of the 535 line are practically independent of the density. Moreover, the values γ_g were found to be almost the same for various foreign gases and varied between $0.048\ \mathrm{cm}^{-1}$ (TlI + Ar) [4] and $0.055\ \mathrm{cm}^{-1}$ (TlI + O_2 and TlI + H_2) [1, 7]. This means that the values γ_g of the resultant Gaussian half-width are significantly greater than the "usual" Doppler half-width γ_d' (or $\gamma_\mathrm{d}^{(\mathrm{th})}$). The difference $\gamma_\mathrm{g} - \gamma_\mathrm{d}'$ (or $\gamma_\mathrm{g} - \gamma_\mathrm{d}^{(\mathrm{th})}$) can thus be regarded as some measure of the additional Doppler broadening resulting from the recoil of the excited Tl atom after photodissociation of the TlI-molecule.

In the present work we assume that the Doppler and pressure broadening are statistically independent. If the correlation between the Doppler and pressure effects is taken into account, then deviations from the Voigt profile giving rise to line asymmetry may occur [23]. The magnitude of this asymmetry depends on the ratio of the mass of the perturber to that of the emitting atom. According to Ward et al. [23] the correlation effects are not expected to be noticeable if the value of this ratio is less than 5. This condition is fulfilled for all perturbers used in our experiments.

4. Cross-Sections for the Broadening and Shift of the 535 nm Tl Line by Foreign Gases

Using the experimental values of collision broadening and shift coefficients β and δ measured in [1–10] (see Table 1) for various gases, the effective cross-sections $\overline{v\sigma_\mathrm{b}}/\bar{v}$ and $\overline{v\sigma_\mathrm{s}}/\bar{v}$ can be determined from (1) and (2) provided the mean relative velocity $\bar{v}$ of the emitter-perturber pair is known. In case of a gas in thermal equilibrium $\bar{v}$ is given by

$$\bar{v} = \bar{v}^{(\mathrm{th})} = \sqrt{\frac{8kT}{\pi}\left(\frac{1}{M} + \frac{1}{m_\mathrm{p}}\right)}, \tag{24}$$

where M is the mass of the emitting Tl-atom and m_p is the mass of the perturber.

Our values of the effective cross-sections $\overline{v\sigma_\mathrm{b}}/\bar{v}^{(\mathrm{th})}$ and $\overline{v\sigma_\mathrm{s}}/\bar{v}^{(\mathrm{th})}$ determined from (1) and (2) using the values of $\bar{v}^{(\mathrm{th})}$ calculated from (24) are listed in Table 2.

In our experiments, however, the assumption of thermal equilibrium is not fully justified because of the recoil of the emitting Tl-atom. For this reason, there may result some uncertainties in the theoretical interpretation if the experimental quantities $\overline{v\sigma_\mathrm{b}}$ and $\overline{v\sigma_\mathrm{s}}$ are expressed in terms of the effective broadening and shift cross-sections $\overline{v\sigma_\mathrm{b}}/\bar{v}^{(\mathrm{th})}$ and $\overline{v\sigma_\mathrm{s}}/\bar{v}^{(\mathrm{th})}$. More accurate data on the mean relative velocity $\bar{v}$ can in principle be obtained from the formula

$$\bar{v} = \langle v \rangle := \langle \sqrt{(\boldsymbol{v}_\mathrm{Tl} - \boldsymbol{v}_\mathrm{p})^2} \rangle, \tag{25}$$

where $\boldsymbol{v}_\mathrm{Tl}$ and $\boldsymbol{v}_\mathrm{p}$ denote the velocities of the Tl-atom and the perturber, respectively. This mean value $\langle v \rangle$ would have to be calculated by means of a distribution function which is itself a product of two distribution functions, one for $\boldsymbol{v}_\mathrm{Tl}$ and another one for $\boldsymbol{v}_\mathrm{p}$. Whereas the distribution of $\boldsymbol{v}_\mathrm{p}$ may be assumed as Maxwellian (and therewith Gaussian, too):

$$\langle v_\mathrm{p} \rangle = \sqrt{\frac{8kT}{\pi m_\mathrm{p}}}, \tag{26}$$

it is not possible to determine the distribution of $\boldsymbol{v}_\mathrm{Tl}$, since some parameters of the TlI-potential curves are not known. Moreover, another complication arises due to the fact that in all experiments

Table 1. Experimental values of collision broadening β and shift δ coefficients (in units $10^{-20}\,\mathrm{cm}^{-1}$/molecule cm^3) for the 535.0 nm Tl line. Units of polarizabilities α are $10^{-24}\,\mathrm{cm}^3$. Numbers in parantheses are standard deviations.

Perturber	α	β	δ	δ/β	Ref.
He	0.216	3.05 (0.03)	+ 0.30 (0.03)	+ 0.099 (0.015)	[5]
Ne	0.398	1.45 (0.02)	− 0.34 (0.02)	− 0.234 (0.014)	[5]
Ar	1.63	3.36 (0.09)	− 0.48 (0.01)	− 0.291 (0.01)	[5]
Kr	2.48	2.96 (0.03)	− 0.95 (0.03)	− 0.32 (0.01)	[4]
Xe	4.01	3.05 (0.03)	− 0.98 (0.03)	− 0.32 (0.01)	[4]
H_2	0.806	3.70 (0.1)	− 0.443 (0.01)	− 0.119 (0.004)	[1], [2]
D_2	0.796	2.84 (0.04)	− 0.64 (0.03)	− 0.225 (0.01)	[3]
O_2*	1.60	3.26 (0.1)	− 1.03 (0.09)	− 0.316 (0.03)	[7], [24]
N_2*	1.76	3.07 (0.06)	− 1.22 (0.04)	− 0.397 (0.015)	[6], [24]
CO_2	2.65	3.99 (0.14)	− 0.944 (0.08)	− 0.237 (0.02)	[8]
SF_6	4.48	5.12 (0.47)	− 1.59 (0.3)	− 0.311 (0.07)	[9]
CO	1.95	3.59 (0.09)	− 1.05 (0.1)	− 0.292 (0.03)	[10]

* Please note that the β and δ values for N_2 and O_2 in [6] and [7] were corrected in the errata [24].

Table 2. The velocity-averaged collision broadening $\overline{v\sigma_\mathrm{b}}/\bar{v}$ and shift $\overline{v\sigma_\mathrm{s}}/\bar{v}$ cross-sections (in units $10^{-14}\,\mathrm{cm}^2$) for the 535.0 nm Tl line for two sets of mean relative velocities. Units: $\bar{v}$ in $10^4\,\mathrm{cm\,s}^{-1}$, $(\alpha/\bar{v})^{2/5}$ in $10^{-12}\,\mathrm{cm}^{4/5}\,\mathrm{s}^{2/5}$.

Perturber	$\bar{v}^{(\mathrm{th})}$	$(\alpha/\bar{v}^{(\mathrm{th})})^{2/5}$	$\overline{v\sigma_\mathrm{b}}/\bar{v}^{(\mathrm{th})}$	$\overline{v\sigma_\mathrm{s}}/\bar{v}^{(\mathrm{th})}$	$\langle v \rangle$	$(\alpha/\langle v \rangle)^{2/5}$	$\overline{v\sigma_\mathrm{b}}/\langle v \rangle$	$\overline{v\sigma_\mathrm{s}}/\langle v \rangle$
He	19.88	1.035	1.45 (0.014)	0.29 (0.03)	20.43	1.023	1.41 (0.014)	0.281 (0.03)
Ne	9.19	1.797	1.48 (0.02)	0.69 (0.04)	10.31	1.717	1.32 (0.02)	0.62 (0.04)
Ar	6.81	3.561	4.64 (0.12)	2.71 (0.03)	8.27	3.295	3.82 (0.1)	2.23 (0.02)
Kr	5.11	4.73	5.45 (0.06)	3.48 (0.11)	6.94	4.182	4.01 (0.04)	2.56 (0.08)
Xe	4.41	6.08	6.52 (0.06)	4.17 (0.13)	6.43	5.222	4.46 (0.04)	2.85 (0.09)
H_2	27.88	1.53	1.25 (0.06)	0.30 (0.007)	28.27	1.52	1.24 (0.04)	0.295 (0.009)
D_2	19.84	1.74	1.35 (0.02)	0.61 (0.08)	20.36	1.727	1.31 (0.02)	0.592 (0.02)
O_2	7.49	3.40	4.09 (0.12)	2.59 (0.23)	8.84	3.186	3.47 (0.11)	2.19 (0.2)
N_2	7.94	3.46	3.66 (0.07)	2.91 (0.09)	9.23	3.253	3.14 (0.06)	2.50 (0.08)
CO_2	6.55	4.41	5.78 (0.2)	2.71 (0.22)	8.05	4.045	4.63 (0.16)	2.19 (0.2)
SF_6	4.27	6.41	11.2 (1.03)	6.97 (1.32)	6.34	5.49	7.57 (0.7)	4.64 (0.9)
CO	7.94	3.61	4.28 (0.11)	2.50 (0.24)	9.22	3.39	3.63 (0.1)	2.12 (0.2)

reported in [1 – 10] the photodissociation of TlI was excited by the three mercury lines: 194.2, 197.2 and 200.2 nm and not by monochromatic light. If, however, the distribution of v_{Tl} is Gaussian – and the experimental results of the Doppler profile in [1 – 10] strongly support this hypothesis – (25) may be replaced by the simpler one

$$\bar{v} = \langle v \rangle := \sqrt{\langle v_{\mathrm{Tl}} \rangle^2 + \langle v_{\mathrm{p}} \rangle^2} \tag{25a}$$

which follows from the addition theorem of the Gaussian normal distribution.

We can calculate $\langle v_{\mathrm{Tl}} \rangle$ using the formula for the usual Doppler half-width (cf. (23)) in which $\gamma_{\mathrm{d}}^{(\mathrm{th})}$ is replaced by the half-width γ_{g} of the Gaussian component of the Voigt-profile of the 535 line. This yields

$$\langle v_{\mathrm{Tl}} \rangle = \frac{c}{v_0 \sqrt{\pi \ln 2}} \gamma_{\mathrm{g}} \, . \tag{27}$$

Eventually, $\bar{v} = \langle v \rangle$ can be calculated by inserting (26) and (27) into (25a). In our case ($T = 733$ K, $\gamma_{\mathrm{g}} \approx 0.05\ \mathrm{cm}^{-1}$ [1 – 10]) $\langle v_{\mathrm{Tl}} \rangle = 5.4 \times 10^4\ \mathrm{cm\ s}^{-1}$; the corresponding values of the mean velocity $\langle v \rangle$ are listed in Table 2. It is seen that the values $\bar{v}^{(\mathrm{th})}$ and $\langle v \rangle$ differ the more, the larger the perturber mass m_{p} is.

The cross-sections $\overline{v\sigma_{\mathrm{b}}}/\langle v \rangle$ and $\overline{v\sigma_{\mathrm{s}}}/\langle v \rangle$ of the 535 line corresponding to the mean relative velocity $\langle v \rangle$ determined from (25a) are connected with the cross-sections $\overline{v\sigma_{\mathrm{b}}}/\bar{v}^{(\mathrm{th})}$ and $\overline{v\sigma_{\mathrm{s}}}/\bar{v}^{(\mathrm{th})}$ corresponding to the thermal mean velocity by

$$\frac{\overline{v\sigma_{\mathrm{b}}}}{\langle v \rangle} = \frac{\bar{v}^{(\mathrm{th})}}{\langle v \rangle} \, \frac{\overline{v\sigma_{\mathrm{b}}}}{\bar{v}^{(\mathrm{th})}} \tag{28}$$

and

$$\frac{\overline{v\sigma_{\mathrm{s}}}}{\langle v \rangle} = \frac{\bar{v}^{(\mathrm{th})}}{\langle v \rangle} \, \frac{\overline{v\sigma_{\mathrm{s}}}}{\bar{v}^{(\mathrm{th})}} \, . \tag{29}$$

The values $\overline{v\sigma_{\mathrm{b}}}/\langle v \rangle$ and $\overline{v\sigma_{\mathrm{s}}}/\langle v \rangle$ determined in this way are listed in Table 2.

In order to compare our experimental values of $\overline{v\sigma_{\mathrm{b}}}/\bar{v}$ and $\overline{v\sigma_{\mathrm{s}}}/\bar{v}$ for different perturbing gases, i.e. for different polarizabilities α and velocities $\bar{v}$, we have plotted $\overline{v\sigma_{\mathrm{b}}}/\bar{v}$ and $\overline{v\sigma_{\mathrm{s}}}/\bar{v}$ as well as the ratio $\overline{v\sigma_{\mathrm{s}}}/\overline{v\sigma_{\mathrm{b}}}$ vs. the parameter $(\alpha/\bar{v})^{2/5}$. Such plots for $\bar{v} = \bar{v}^{(\mathrm{th})}$ are shown in Figs. 1, 2, and 3. Analogous plots for $\bar{v} = \langle v \rangle$, made on the basis of (28) and (29) are shown in Figs. 4, 5, and 6.

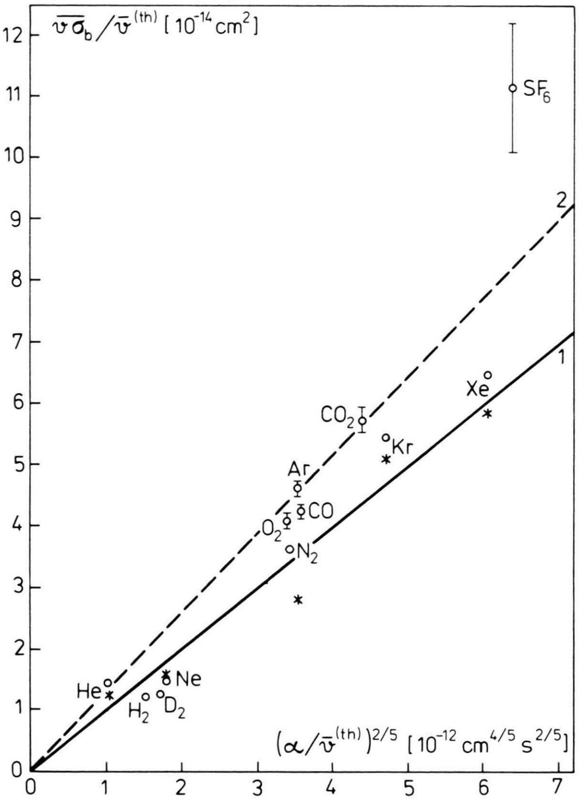

Fig. 1. Broadening cross-section $\overline{v\sigma_{\mathrm{b}}}/\bar{v}^{(\mathrm{th})}$ for the 535.0 nm Tl line perturbed by various foreign gases vs. $(\alpha/\bar{v}^{(\mathrm{th})})^{2/5}$. 1 ——: theoretical Van der Waals dependence calculated from (18) for $\bar{v} = \bar{v}^{(\mathrm{th})}$; 2 – – –: least-squares fit according to (30); $*$: theoretical values calculated from (16) with Lennard-Jones potentials for $\bar{v} = \bar{v}^{(\mathrm{th})}$; ○ experimental values.

Such plots allow for direct comparison of theoretical values of $\sigma_{\mathrm{b}}(\bar{v})$ and $\sigma_{\mathrm{s}}(\bar{v})$ resulting from (16), (17) for the Lennard-Jones potential or (18), (19) for the Van der Waals potential with the experimental values. The values of the polarizabilities α for which the plots in Figs. 1 – 6 were made are listed in Table 1. For H_2 and D_2 we used the theoretical values calculated by Kolos and Wolniewicz [25]. For all other perturbing gases we used the experimental values of α given in [26].

According to (18) and (19) for the Van der Waals potential the impact theory predicts a linear dependence of both $\sigma_{\mathrm{b}}(\bar{v})$ and $\sigma_{\mathrm{s}}(\bar{v})$ on $(\alpha/\bar{v})^{2/5}$.

As it is seen the broadening and shift by Xe, Kr, Ar, O_2, N_2 as well as Ne, H_2, D_2 are in a quite reasonable agreement with those resulting from the impact theory for the Van der Waals potential both in the case of $\bar{v} = \bar{v}^{(\mathrm{th})}$ (Figs. 1 and 2) and of $\bar{v} = \langle v \rangle$

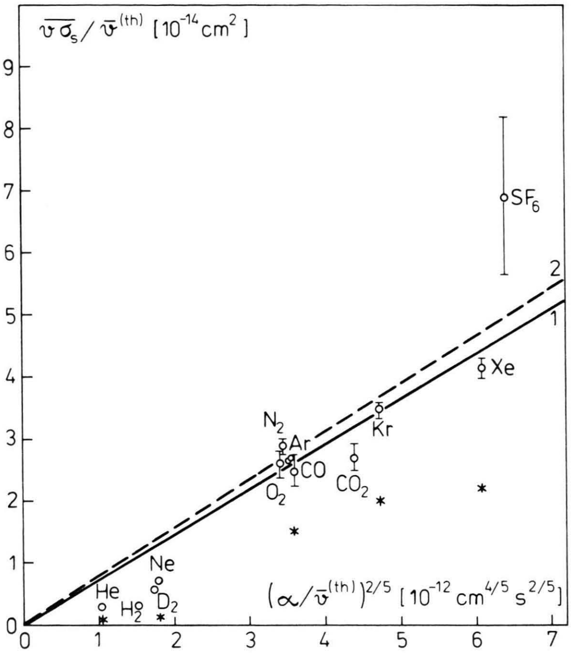

Fig. 2. Shift cross-sections $\overline{v\sigma_s}/\bar{v}^{(\mathrm{th})}$ for the 535.0 nm Tl line vs. $(\alpha/\bar{v}^{(\mathrm{th})})^{2/5}$. 1 ——: theoretical (Van der Waals) dependence according to (19) for $\bar{v}=\bar{v}^{(\mathrm{th})}$; 2 – – –: the least-squares fit according to (32); ∗: theoretical values calculated from (17) with Lennard-Jones potentials for $\bar{v}=\bar{v}^{(\mathrm{th})}$; ○: experimental values.

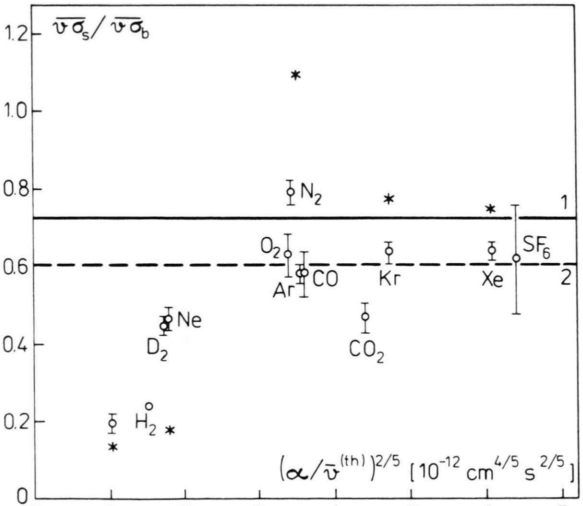

Fig. 3. $\overline{v\sigma_s}/\overline{v\sigma_b}$ vs. $(\alpha/\bar{v}^{(\mathrm{th})})^{2/5}$. 1 ——: constant value 0.727 for the Van der Waals potential; 2 – – –: constant value 0.610 resulting from linear least-squares fits according to (30) and (32); ∗: theoretical values for the Lennard-Jones potentials; ○: experimental values.

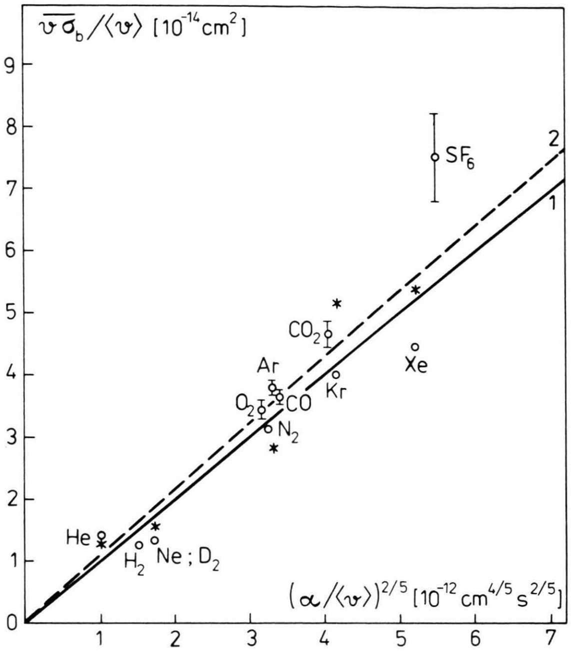

Fig. 4. Broadening cross-sections $\overline{v\sigma_b}/\langle v\rangle$ vs. $(\alpha/\langle v\rangle)^{2/5}$. For the notation see Figure 1.

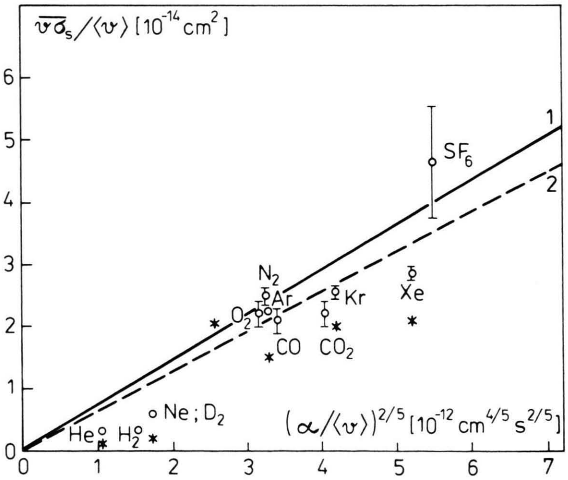

Fig. 5. Shift cross-sections $\overline{v\sigma_s}/\langle v\rangle$ vs. $(\alpha/\langle v\rangle)^{2/5}$. Notation as in Figure 2.

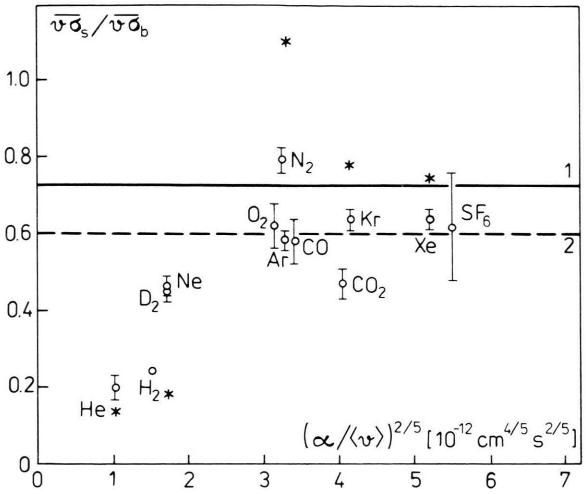

Fig. 6. $\overline{v\sigma_s}/\overline{v\sigma_b}$ vs. $(\alpha/\langle v\rangle)^{2/5}$. Notation as in Figure 3. 2 – – –: constant value 0.604.

(Figs. 4 and 5). For polyatomic the molecules SF_6 and CO_2 the agreement is poor. We have found, however, that all experimental values of $\overline{v\sigma_b}/\bar{v}$ and $\overline{v\sigma_s}/\bar{v}$ may still be better interpreted by the straight lines marked by 2 in Figures 1–6, which represent a linear least-squares fit of the data. The equation of the straight line 2 in Fig. 1 is

$$\frac{\overline{v\sigma_b}}{\bar{v}^{(\mathrm{th})}} = A\left(\frac{\alpha}{\bar{v}^{(\mathrm{th})}}\right)^{2/5}. \tag{30}$$

Using the least-squares method we obtained for A the value $1.28 \times 10^{-2}\ \mathrm{cm}^{6/5}\ \mathrm{s}^{-2/5}$.

The linear fit represented in Fig. 4 by the straight line 2 is

$$\frac{\overline{v\sigma_b}}{\langle v\rangle} = 1.07 \times 10^{-2}\ \mathrm{cm}^{6/5}\ \mathrm{s}^{-2/5}\left(\frac{\alpha}{\langle v\rangle}\right)^{2/5}. \tag{31}$$

It should be noted that these linear least-squares fittings were performed taking into account all experimental values of $\overline{v\sigma_b}/\bar{v}^{(\mathrm{th})}$ or $\overline{v\sigma_b}/\langle v\rangle$ except those for the broadening by helium. The points marked by * in Figs. 1 and 4 are the theoretical values of $\sigma_b(\bar{v}^{(\mathrm{th})})$ and $\sigma_b(\langle v\rangle)$, respectively, computed from (16) for He, Ne, Ar, Kr and Xe assuming Lennard-Jones potentials. The values of the C_{12} parameters were taken from our previous papers on thallium-noble gas systems (see Table 3 in [4, 5]). No calculations based on the Lennard-Jones potential were performed for molecular perturbers because the corresponding parameters C_{12} are not known.

Figures 2 and 5 show measured values of $\overline{v\sigma_s}/\bar{v}^{(\mathrm{th})}$ and $\overline{v\sigma_s}/\langle v\rangle$ vs. $\sigma_s(\bar{v}^{(\mathrm{th})})$ and $\sigma_s(\langle v\rangle)$, respectively. As it is seen the experimental values for perturbing gases with higher polarizability (Ar, Kr, Xe, N_2, O_2, CO, CO_2 and SF_6) are in fairly good agreement with those calculated from the impact theory for the Van der Waals potential.

An agreement of experimental values of $\overline{v\sigma_b}/\bar{v}$ and $\overline{v\sigma_s}/\bar{v}$ for the 535 line perturbed by CO with calculations based on the Van der Waals potential should be surprising since CO is a molecule with permanent electric-dipole moment. Evidently CO behaves in the collisional broadening and shift phenomena as if it were non-polar. A similar behaviour of CO was recently observed by Kachru et al. [27] in their experiments on the CO-induced collision broadening of spectral lines involving highly excited Rydberg states of sodium. They found good agreement of measured values for Na perturbed by CO with those calculated from the Omont theory [28] of collision effects on Rydberg atoms developed for non-polar perturbing gases.

The straight lines marked by 2 in Figs. 2 and 5 represent least-squares fits of the shift data according to the relations

$$\frac{\overline{v\sigma_s}}{\bar{v}^{(\mathrm{th})}} = 7.81 \times 10^{-3}\ \mathrm{cm}^{6/5}\ \mathrm{s}^{-2/5}\left(\frac{\alpha}{\bar{v}^{(\mathrm{th})}}\right)^{2/5} \tag{32}$$

and

$$\frac{\overline{v\sigma_s}}{\langle v\rangle} = 6.46 \times 10^{-3}\ \mathrm{cm}^{6/5}\ \mathrm{s}^{-2/5}\left(\frac{\alpha}{\langle v\rangle}\right)^{2/5}. \tag{33}$$

As in the case of broadening, we have omitted in these fittings the He-data because the Van der Waals potential, for which the linear dependence of $\sigma_b(\bar{v})$ and $\sigma_s(\bar{v})$ on $(\alpha/\bar{v})^{2/5}$ is a typical feature, cannot explain even the sign of the shift (towards the blue) caused by helium.

In Figs. 3 and 6 the experimental values of the ratio $\overline{v\sigma_s}/\overline{v\sigma_b}$ for the 535 line are plotted vs. $(\alpha/\bar{v})^{2/5}$ and compared with theoretical values for Lennard-Jones potentials (points *) and with the constant value 0.727 resulting from the impact theory for Van der Waals interaction.

The values of the ratio $\overline{v\sigma_s}/\overline{v\sigma_b}$ determined from the linear fits given by (30), (32) and (31), (33) are 0.610 and 0.604, respectively; they differ but little from the theoretical Van der Waals value. The ratio

$\overline{v\sigma_s}/\overline{v\sigma_b}$ is a very good test of interaction potentials. As it is seen from Figs. 3 and 6, the largest discrepancies between real potentials and Van der Waals type potentials should occur for light perturbing gases (He, Ne, H_2, D_2), in agreement with other observations (cf. [11–15], [29–31]).

The discrepancy between the Van der Waals theoretical line 1 in Figs. 1 and 4 and that (line 2) obtained from the linear fitting ((30) or (32)) can be reduced if all Van der Waals parameters ΔC_6 for the 535 line perturbed by different foreign gases are increased by a factor $\eta^{5/2}$, where η is the ratio of the fitting parameter $A = 1.28 \times 10^{-2}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}$ (or $A = 1.07 \times 10^{-2}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}$) in (30) (or (31)) to the theoretical coefficient $9.98 \times 10^{-3}\,\mathrm{cm}^{6/5}\,\mathrm{s}^{-2/5}$ in (18). We thus found that the ΔC_6 parameters should be increased by a factor of 1.86 in the case of $v = \bar{v}^{(\mathrm{th})}$ or by a factor of 1.19 for $\bar{v} = \langle v \rangle$.

A procedure in which the discrepancy between the theoretical broadening values and experimental data is reduced by simply increasing C_6 was often used in the past ([29], cf. also [16, 30]). Such a procedure, however, was criticized by Roueff and van Regemorter [31] who have shown that in some cases, especially for light perturbers, it leads to empirical C_6 values which are much too big compared to the theoretical values.

In the present work, the theoretical C_6 values used to derive (18) and (19) for the broadening and shift cross-sections $\bar{\sigma}_b$ and $\bar{\sigma}_s$ for the 535 line were calculated from the Unsöld formula (9) with $\langle r^2 \rangle$ computed from the Coulomb approximation (15). In [4] and [5] $\langle r^2 \rangle$-values were also calculated for Tl using the Hartree-Fock wave functions evaluated from the computer program given by Froese-Fischer [34]. They lead to ΔC_6 values which are greater by a factor of 1.34 for Tl + Ar and Tl + Xe and 1.36 for Tl + Kr than those calculated from the Coulomb approximation.

On the other hand, however, to reduce the discrepancy between the Van der Waals straight line $\sigma_s(\langle v \rangle)$ (line 1 in Fig. 5) and the linear fit $\overline{v\sigma_s}/\langle v \rangle$ based on (33) (line 2 in Fig. 5) the Van der Waals parameters ΔC_6 should be decreased by a factor of 0.75. In the case of the mean relative velocity $\bar{v} = \bar{v}^{(\mathrm{th})}$ they should be increased by a factor of 1.20. Thus we can conclude that it is not possible to interpret in a consistent way – even for foreign gases with high polarizability – the broadening and shift data using a Van der Waals potential alone, although in some cases the agreement with experiment is fairly good. This type of the potential is completely inadequate both for the shift and broadening for light perturbers, i.e. with low polarizability α. As was theoretically shown by Reck and Hood [32] and confirmed experimentally by some workers (cf. e.g. [33]), the shift is very sensitive to the details of the interaction potential in the upper and lower states of the emitting atom and to the procedure used in calculating it. On the other hand, the broadening is overwhelmingly determined by the long range potential in the upper state, and this circumstance could explain a reasonable agreement between the Van der Waals parameters ΔC_6 calculated from the Hartree-Fock approximation and those determined from the linear least-squares fit to the broadening data.

5. Conclusion

An accurate interpretation of experimental data on the pressure broadening and shift of the 535.0 nm Tl fluorescence line emitted due to the photodissociation of TlI-molecules requires the knowledge of the recoil velocity distribution. In the present paper we have performed an approximate interpretation based on some estimations of the mean relative velocities. We have shown that the variation of collisional broadening and shift cross-sections $\overline{v\sigma_b}/\bar{v}$ and $\overline{v\sigma_s}/\bar{v}$ for the same spectral line perturbed by various foreign gases with the quantity $(\alpha/\bar{v})^{2/5}$ may serve as an additional source of information on the interaction between the emitting atom and perturbing particles. The plots of $\overline{v\sigma_b}/\bar{v}$, $\overline{v\sigma_s}/\bar{v}$ and their ratio $\overline{v\sigma_s}/\overline{v\sigma_b}$ versus $(\alpha/\bar{v})^{2/5}$ clearly demonstrate a departure of the real interaction potential from the Van der Waals potential. Calculations performed on the basis of the Lindholm-Foley theory for the Lennard-Jones potential indicate that the inclusion of the repulsion part in the interaction energy is necessary not only for helium but also for other light perturbers like Ne, H_2, and D_2.

[1] E. Lisicki, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. A **56,** 557 (1979).

[2] E. Lisicki, Z. Naturforsch. **35a,** 773 (1980).

[3] E. Lisicki, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. A **58,** 105 (1980).

[4] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **35a,** 1249 (1980).

[5] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **36a,** 807 (1981).

[6] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **37 a,** 93 (1982).

[7] E. Lisicki, A. Bielski, and J. Szudy, Z. Naturforsch. **37a,** 1094 (1982).

[8] E. Lisicki, A. Bielski, R. S. Dygdala, and J. Szudy, Acta Phys. Polon. A **61,** 421 (1982).

[9] E. Lisicki, R. Bobkowski, J. Szudy, and J. Wolnikowski, Z. Naturforsch. **38a,** 838 (1983).

[10] E. Lisicki, A. Bielski, D. Bilińska, J. Szudy, and J. Wolnikowski, Acta Phys. Polon. A **65,** 361 (1984).

[11] F. Schuller and W. Behmenburg, Phys. Lett. C **12,** 273 (1974).

[12] N. Allard and J. Kielkopf, Rev. Mod. Phys. **54,** 1103 (1982).

[13] I. I. Sobelman, Introduction to the Theory of Atomic Spectra, Pergamon Press, Oxford 1972.

[14] A. Spielfiedel and E. Roueff, J. Phys. B **14,** L 795 (1981).

[15] A. Unsöld, Physik der Sternatmosphären, Springer-Verlag, Berlin 1955.

[16] W. R. Hindmarsh, A. D. Petford, and G. Smith, Proc. Roy. Soc. London A **297,** 296 (1967).

[17] D. N. Stacey and J. Cooper, J. Quant. Spectrosc. Radiat. Transfer **11,** 1271 (1971).

[18] H. G. Kuhn, Atomic Spectra, Longmans, Green and Co., Ltd., London 1969.

[19] A. Bielski, S. K. Kandela, J. Wolnikowski, and Z. Turło, Acta Phys. Polon. A **42,** 295 (1972).

[20] A. Bielski, W. Dokurno, E. Lisicki, and Z. Turło, Optica Applicata **11,** 151 (1981).

[21] R. N. Zare and D. R. Herschbach, Proc. IEEE **51,** 173 (1963).

[22] K. P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 4. Constants of Diatomic Molecules, Van Nostrand Reinhold Co., New York 1979.

[23] J. Ward, J. Cooper, and E. W. Smith, J. Quant. Spectr. Radiat. Transfer **14,** 555 (1974).

[24] E. Lisicki, A. Bielski, and J. Szudy, Errata to [6] and [7], Z. Naturforsch. **38a,** 1048 (1983).

[25] W. Kołos and L. Wolniewicz, J. Chem. Phys. **46,** 1426 (1967).

[26] Landoldt-Börnstein, Zahlenwerte und Funktionen, Atom- and Molekularphysik, Vol. I, Berlin 1950.

[27] R. Kachru, T. W. Mossberg, and S. R. Hartmann, Phys. Rev. A **22,** 1953 (1980).

[28] A. Omont, J. Phys. Paris **38,** 1343 (1977).

[29] H. Holweger, Astro. Astrophys. **10,** 128 (1971).

[30] W. R. Hindmarsh, A. N. du Plessis, and J. M. Farr, J. Phys. B **3,** L 5 (1970).

[31] E. Roueff and H. van Regemorter, Astro. Astrophys. **12,** 317 (1971).

[32] G. P. Reck and R. J. Hood, J. Chem. Phys. **56,** 1230 (1972).

[33] G. H. Copley, J. Quant. Spectrosc. Radiat. Transfer **16,** 377 (1976).

[34] C. Froese-Firscher, Comput. Phys. Commun. **4,** 107 (1972).