

C. VADLA^{1,✉}
V. HORVATIC¹
K. NIEMAX²

Accurate determination of the atomic number density in dense Cs vapors by absorption measurements of Cs₂ triplet bands

¹ Institute of Physics, Bijenicka 46, 10000 Zagreb, Croatia

² ISAS – Institute for Analytical Sciences, Bunsen-Kirchhoff-Strasse 11, 44139 Dortmund, Germany

Received: 9 January 2006/Revised version: 21 April 2006

Published online: 24 June 2006 • © Springer-Verlag 2006

ABSTRACT The spectra of Cs metal vapor have been experimentally investigated by spatially resolved absorption in overheated cesium vapor generated in a heat pipe oven. The reduced absorption coefficients of the triplet satellite bands at 875.5 nm and the diffuse band between 705 nm and 720 nm were found to be independent of temperature in the range between 600 K and 1000 K. The absorption data of these molecular features can be successfully used for very simple and accurate Cs number density determination in the range from about $5 \times 10^{17} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$.

PACS 33.20.Ea; 33.20.Kf; 33.70.Fd

1 Introduction

The accurate and precise determination of atomic number densities in dense metal vapors is a very difficult task. Provided that reliable vapor pressure curves are available there is always the problem of measuring correctly the temperatures of the mostly liquid metal and of the vapor phase. Therefore, it is advantageous to determine the atomic density by spectroscopic means, e.g., by absorption. In the present experiment Cs number densities had to be measured up to 10^{18} cm^{-3} . At such conditions, and with the typical absorption column length L of the order of about 10 cm, the standard absorption spectroscopy methods using optically thin lines are not applicable. The use of optically thick lines in combination with the curve of growth method [1] is inaccurate, due to the uncertainties in the relevant line broadening parameters. In addition, the knowledge of the vapor temperature is necessary for the application of the curve of growth method which makes it even more complicated. As was shown in [2], the extended quasistatic resonance line wings can be successfully used as a straightforward and very reliable standard for determination of relatively high (up to about 10^{17} cm^{-3}) number densities in alkali vapors. The absorption coefficients k in the

wings of the resonance lines are insensitive to temperature and its absolute value is directly proportional to the square of the atom number density N . Extensive experimental and theoretical studies yielded accurate results for the values of the corresponding reduced absorption coefficients $k_R(\lambda) = k(\lambda)/N^2$ for Cs, Rb, K, and Na. However, for number densities higher than 10^{17} cm^{-3} this method becomes inaccurate due to molecular background absorption in the spectra.

On the other hand, many relatively narrow (several nanometers), spectrally isolated and optically thin molecular bands are measurable in the range of cesium number densities from $5 \times 10^{16} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$. Following the semiclassical approach, the absorption coefficient of a molecular band can be expressed as $k \propto N^2 \exp[-\Delta V_1(R)/k_B T]$, where the energy difference $\Delta V_1(R)$ of the lower dimer potential curve at the internuclear distance R is given by $V_1(R) - V_1(\infty)$. Molecular bands stemming from the shallow ground states ($\Delta V \ll k_B T$), for instance the alkali triplet states, are good candidates for the determination of atomic number densities since they depend only weakly on temperature. For the case of potassium triplet bands, this possibility was already pointed out in [3] and analyzed in details in [4]. Following this approach, the resonance line satellite band at 875.5 nm and the diffuse band appearing in the spectral range 704 nm to 720 nm have been chosen as the most convenient Cs triplet bands for Cs number density determination. The temperature dependence of these bands was investigated in strongly overheated vapor, and their absolute strengths in terms of reduced absorption coefficients were calibrated using the accurate values for cesium resonance line wings.

2 Experiment and quantitative analysis of the data

2.1 Experimental details

The specific details of our simple experimental arrangement are given in [4] and will be repeated here only briefly. The cesium vapor column (length: $6.5 \pm 0.5 \text{ cm}$) was produced in a stainless-steel heat pipe (inner diameter: 2 cm, length: 18 cm). Argon was used as a buffer gas to protect the quartz windows from the corrosive influence of the hot metal vapor. The cesium vapor was generated by an outer heater

✉ Fax: +385-1-469-8889, E-mail: vadla@ifs.hr

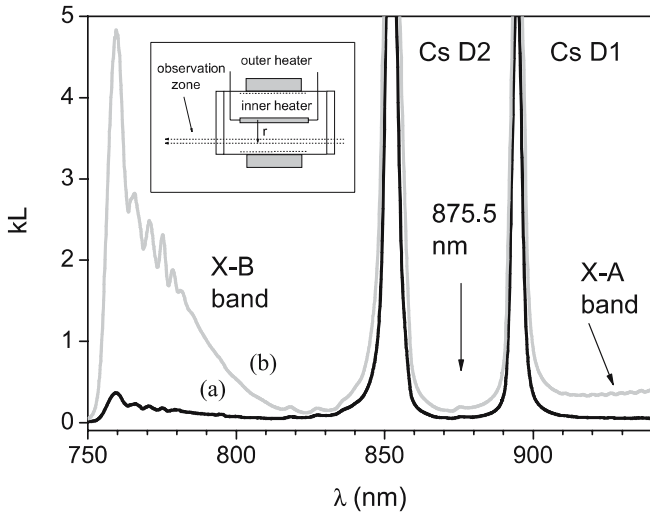


FIGURE 1 Measured optical depths kL in strongly overheated cesium vapor at positions $r = 2$ mm (a) and $r = 9$ mm (b) from the heat pipe axis. The applied outer and inner heating powers were 130 W and 10 W, respectively. The buffer gas pressure was 5 mbar

and overheated with the help of an inner heater built in along the heat pipe axis (see inset of Fig. 1). The inner heater in Fig. 1 was a 250 μm thick molybdenum wire wound up in helix form (about 1 winding per mm) with an outer diameter of 2 mm and 12 mm in length. Molybdenum was chosen because of its resistance to hot dense cesium vapor, which was found to be better in comparison with properties of other materials at our disposal (including tungsten). The helix was fixed at both ends to the supports inserted through the heat pipe wall and slightly strained. In this manner the change of the wire length during the heating was compensated by elastic properties of the helix, thus preventing the droop of the heater. Throughout the measurement the heater remained stretched in full length at the heat pipe axis, which ensured the axial symmetry. The heat pipe operated in the heat pipe mode, i.e., the cesium pressure was equal to the buffer gas pressure. In first order, the temperature and consequently the vapor number density distributions were axially symmetric. The temperature was ranging from T_c at the radius $r_c = 1$ mm of the inner heater to the metal bath temperature T_w at the heat pipe wall ($r_w = 10$ mm). The boundary temperatures depended on the inner and outer heating powers applied. In the present experiment, the typical values for T_c and T_w were about 1000 and 600 K, respectively. Strongly overheated and radially inhomogeneous vapor column was investigated applying white light absorption with spatial resolution. A 0.5 m Jarrel–Ash monochromator supplied with a RCA 7102 photomultiplier (S-1 cathode) cooled thermoelectrically down to -20 $^{\circ}\text{C}$ was used to analyse the spectra. The spectral resolution was 0.3 nm, which was much smaller than the width of the investigated spectral bands. The spatially resolved absorption spectra were related to thin columns (diameter $\Delta r \approx 0.5$ mm) at the distance r from the heat pipe axis.

2.2 Line wings of the resonance lines

Typical spectra obtained at lower Cs number densities are shown in Fig. 1. As already mentioned in the intro-

duction, the quantitative analysis is based on the accurate data of the absorption coefficient in the quasistatic line wings. According to [2, 5], the absorption coefficient $k_{D1}(\Delta\lambda)$ in the red wing of the cesium D1 line can be expressed as

$$k_{D1}^{\text{red}}(\Delta\lambda) = 9.46 \times 10^{-32} P(\Delta\lambda/\Delta_{fs}) \frac{N^2}{(\Delta\lambda)^2}. \quad (1)$$

Here, the absorption coefficient is given in cm^{-1} with N and the detuning $\Delta\lambda$ from the D1 line center expressed in cm^{-3} and nanometers, respectively. The polynomial $P(\Delta\lambda/\Delta_{fs})$ reads

$$P(\Delta\lambda/\Delta_{fs}) = 1.0317 + 2.2934 \left(\frac{\Delta\lambda}{\Delta_{fs}}\right) - 0.6319 \left(\frac{\Delta\lambda}{\Delta_{fs}}\right)^2 + 0.0732 \left(\frac{\Delta\lambda}{\Delta_{fs}}\right)^3, \quad (2)$$

where the Δ_{fs} is the fine structure splitting of the cesium first resonance doublet (42.6 nm). It should be pointed out that (2) can be applied for detunings $1 \text{ nm} \leq \Delta\lambda \leq 3\Delta_{fs}$.

As one can see in Fig. 1, at dense vapor conditions the resonance lines are superimposed on the molecular background, which should be subtracted from the measured total optical depth $k(\lambda)L$. This procedure is sketched in Fig. 2, where the shape of the X-A molecular band in the vicinity of the Cs D1 line is approximated by straight lines. The height and the slope of the straight lines were fitted to the values for which the remaining optical depths $k(\Delta\lambda)L$ acquired the wavelength dependence defined by (1) and (2). Then, by using (1) and (2) and the estimated value for the column length L , one obtains corresponding values for the number densities $N(r)$ at given distances r .

The measurements were performed from $r = 2$ mm (near the inner heater) to $r = 9$ mm (near the heat pipe wall). The number density $N(r_w = 10 \text{ mm})$ just above the bath of the liquid cesium in the stainless-steel mesh at the heat pipe

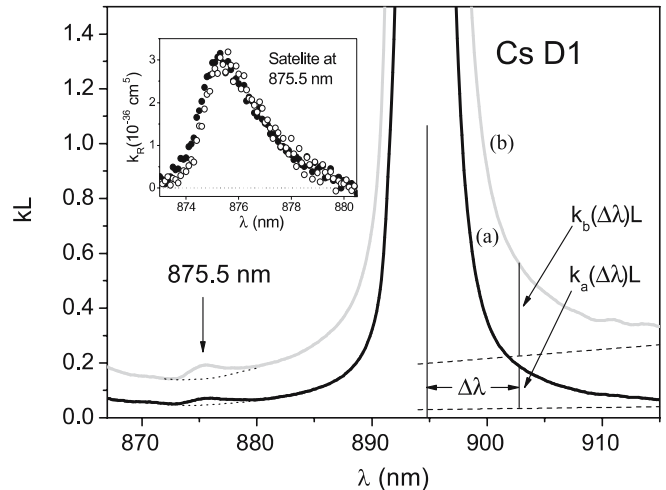


FIGURE 2 The vicinity of the Cs D1 line recorded at the same experimental conditions as in Fig. 1. Dashed lines represent the estimated X-A molecular backgrounds. Inset: the reduced absorption coefficient of the 875.5 nm satellite measured at $T_a = 920$ K (full circles) and $T_b = 610$ K (open circles). See the text for further explanations

wall was determined by extrapolation. The temperature T_w of the liquid metal bath, being in thermal equilibrium with vapor above its surface was determined using the cesium atomic vapor pressure curve [6]. According to [6], the number density of cesium dimers is negligible in comparison with the atomic number density at the present experimental conditions. The temperature $T(r)$ at a chosen position r can be calculated using ideal gas law which yields $T(r) = T(r_w)N(r)/N(r_w)$. In the case presented in Figs. 1 and 2, the cesium number densities and temperatures were $N_a = 3.4 \times 10^{16} \text{ cm}^{-3}$, $T_a = 920 \text{ K}$ at the position $r_a = 2 \text{ mm}$, and $N_b = 5.1 \times 10^{16} \text{ cm}^{-3}$, $T_b = 610 \text{ K}$ at $r_b = 9 \text{ mm}$. The accuracy of the data is about 4% due to the uncertainty of the vapor column length. The effective column length L was determined by measuring the length of the cesium layer deposited on the inner heater while the inner heating was turned off. As it will be shown below, the uncertainty of the vapor column length does not influence the final results but only introduces an error in the determination of the temperatures.

2.3 The satellite band at 875.5 nm

The satellite band at 875.5 nm lies on a background related to the inner wings of the cesium resonance doublet and the blue tail of the Cs_2 X-A band. This continuous background can be easily subtracted from the total absorption coefficient of the satellite (dotted lines in Fig. 2). Thus, the optical depth of the satellite band was measured relative to the optical depth of the red wing of the Cs D1 line. This procedure cancels out the uncertainties due to the vapor column length L and yields the corresponding reduced absorption coefficient k_R by using (1) and (2) to express k_{D1} . As can be seen in the inset of Fig. 2, the reduced absorption coefficient of the 875.5 nm band is independent of temperature within the experimental error bars. The peak value at 875.5 nm was found to be

$$k_R(875.5) = (2.9 \pm 0.3) \times 10^{-36} \text{ cm}^5, \tag{3}$$

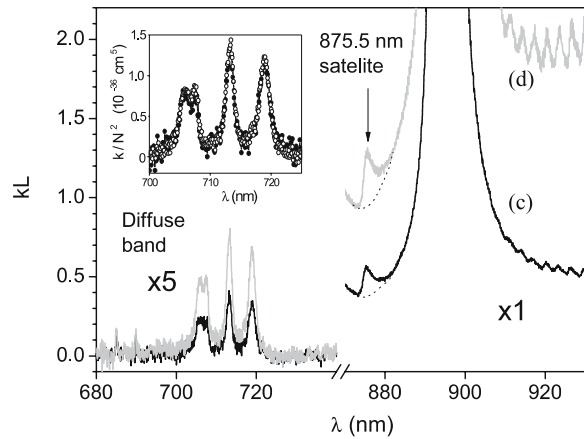


FIGURE 3 Absorption spectrum of the cesium diffuse band together with the spectrum of the Cs D1 line at radial positions $r = 2 \text{ mm}$ (c) and $r = 9 \text{ mm}$ (d). The applied outer and inner heating powers were 160 W and 12 W, respectively, and the buffer gas pressure was 15 mbar. The corresponding cesium number densities are $N_c = 9.5 \times 10^{16} \text{ cm}^{-3}$ and $N_d = 1.3 \times 10^{17} \text{ cm}^{-3}$. Inset: The reduced absorption coefficient of the cesium diffuse band at $T_c = 1020 \text{ K}$ (full circles) and $T_d = 740 \text{ K}$ (open circles).

for temperatures between 600 K and 900 K. Averaged values of the reduced absorption coefficient in the region between 873 and 880 nm are given in Table 1.

2.4 Diffuse band between 704 nm and 720 nm

The diffuse band with three distinct peaks at 707 nm, 713 nm and 719 nm becomes measurable at $N \approx 10^{17} \text{ cm}^{-3}$. This is illustrated in Fig. 3, where the diffuse band is plotted together with the Cs D1 line. As mentioned before, the determination of the cesium number density using the wings of the resonance lines becomes inaccurate at such conditions. Therefore, the data for the temperature independent reduced absorption coefficient of the 875.5 nm satellite was used to perform the quantitative analysis, i.e., for the evaluation of the reduced absorption coefficient of the diffuse band. The result of the analysis has shown (see inset of Fig. 3) that

λ (nm)	k_R	λ (nm)	k_R	λ (nm)	k_R	λ (nm)	k_R
873	0.18022	875	2.67948	877	1.61618	879	0.43036
873.1	0.19076	875.1	2.82053	877.1	1.46995	879.1	0.43102
873.2	0.17361	875.2	2.91252	877.2	1.385	879.2	0.36937
873.3	0.20452	875.3	2.89282	877.3	1.31777	879.3	0.37254
873.4	0.2375	875.4	2.93355	877.4	1.20238	879.4	0.34776
873.5	0.26849	875.5	2.92387	877.5	1.14922	879.5	0.25573
873.6	0.32159	875.6	2.80339	877.6	1.08748	879.6	0.23827
873.7	0.39615	875.7	2.76247	877.7	0.99252	879.7	0.18852
873.8	0.43382	875.8	2.73188	877.8	0.9489	879.8	0.1329
873.9	0.51978	875.9	2.58376	877.9	0.90284	879.9	0.13044
874	0.63336	876	2.52258	878	0.8123	880	0.12283
874.1	0.71273	876.1	2.45657	878.1	0.79051		
874.2	0.88136	876.2	2.33744	878.2	0.73561		
874.3	1.09887	876.3	2.23761	878.3	0.62302		
874.4	1.29764	876.4	2.14116	878.4	0.62122		
874.5	1.548	876.5	1.98356	878.5	0.60538		
874.6	1.84963	876.6	1.93784	878.6	0.50577		
874.7	2.06389	876.7	1.86298	878.7	0.51378		
874.8	2.29846	876.8	1.75742	878.8	0.51177		
874.9	2.5252	876.9	1.69522	878.9	0.43099		

TABLE 1 The reduced absorption coefficient of the cesium satellite band at 875.5 nm (in units 10^{-36} cm^5) in dependence on the wavelength

the reduced absorption coefficient of the diffuse band is practically temperature independent in a wide temperature range, similar as in case of the satellite band at 875.5 nm. In the range from 700 K to 1000 K, the reduced absorption peaks at 707 nm, 713 nm and 719 nm were found to be

$$k_R(707) = (0.85 \pm 0.1) \times 10^{-36} \text{ cm}^5,$$

$$k_R(713) = (1.35 \pm 0.1) \times 10^{-36} \text{ cm}^5,$$

$$k_R(719) = (1.2 \pm 0.1) \times 10^{-36} \text{ cm}^5.$$

Averaged values of the reduced absorption coefficient in the region between 700 nm and 725 nm are given in Table 2.

3 Discussion and conclusions

Molecular transitions in alkali vapors have been subject to many experimental and theoretical studies [7], in order to understand various interaction processes between atoms at long-, intermediate- and short-range internuclear distances and to explore possible practical applications. In particular, the triplet molecular bands, i.e., the bands arising from transitions between the repulsive (at short internuclear distances) and weakly bound (at intermediate and long distances) $^3\Sigma_u^+$ ground state is of special interest. In the case of cesium, the first detailed investigations of the temperature dependence of the triplet molecular transitions were made almost thirty years ago [8, 9]. However, the complete identification and theoretical simulation of the triplet transitions was made much

later. This was accomplished by the use of reliable ab initio calculations of the relevant potentials carried out during the last decade (see [10–12] and references therein).

According to [10], the cesium satellite band at 875.5 nm is due to transitions from the $\text{Cs}_2\ ^3\Sigma_u^+$ ground state (Hunds case (c), coupling designation: 0_u^+) to the 0_g^+ state belonging to the $\text{Cs}(6S_{1/2}) + \text{Cs}(6P_{1/2})$ asymptote. The satellite is due to an extremum in the differential potential curve at the internuclear distance of about 19 a.u. (1 nm) where the corresponding binding energy of the ground state is $\Delta V \approx 80 \text{ cm}^{-1}$. As shown in [11], the distinct peaks of the diffuse band at 707 nm, 713 nm and 719 nm are due to transitions from the triplet ground state to the 2_g , 1_g , and 0_g^{+-} states, respectively, which dissociate into $\text{Cs}(6S_{1/2}) + \text{Cs}(5D_{1/2,3/2})$. These peaks are due to double maxima in the difference potentials at internuclear distances around 11 a.u. (0.58 nm) where $\Delta V \approx 120 \text{ cm}^{-1}$. These data are in accordance with our experimental findings regarding the temperature dependence of the investigated triplet features. In the range $(800 \pm 200) \text{ K}$, the corresponding Boltzmann factors $\exp(-\Delta V/k_B T)$ change less than $\pm 10\%$, which is within the error bars of the reduced absorption coefficients measured here.

In order to check the overall accuracy of the proposed method for the determination of the cesium number density, we have measured the reduced absorption coefficient in the wings of the third ($\text{Cs } 6S_{1/2} \rightarrow \text{Cs } 8P_J$) and fourth ($\text{Cs } 6S_{1/2} \rightarrow \text{Cs } 9P_J$) the principal series lines of Cs and used the diffuse band for the determination of the cesium number

λ (nm)	k_R	λ (nm)	k_R	λ (nm)	k_R	λ (nm)	k_R
700	0.02337	707	0.715	714	0.79734	721	0.18732
700.2	0.02795	707.2	0.78495	714.2	0.64626	721.2	0.15289
700.4	0.02596	707.4	0.8785	714.4	0.50551	721.4	0.13091
700.6	0.03453	707.6	0.77515	714.6	0.39662	721.6	0.10731
700.8	0.0464	707.8	0.71443	714.8	0.31966	721.8	0.09532
701	0.05824	708	0.56426	715	0.27258	722	0.08665
701.2	0.06194	708.2	0.47506	715.2	0.23901	722.2	0.07698
701.4	0.06673	708.4	0.38482	715.4	0.23098	722.4	0.0616
701.6	0.067	708.6	0.3036	715.6	0.22162	722.6	0.05129
701.8	0.07149	708.8	0.23647	715.8	0.21812	722.8	0.04812
702	0.08015	709	0.20433	716	0.23993	723	0.04167
702.2	0.08598	709.2	0.18807	716.2	0.25762	723.2	0.03737
702.4	0.08151	709.4	0.18136	716.4	0.27186	723.4	0.03532
702.6	0.09028	709.6	0.17874	716.6	0.28843	723.6	0.02781
702.8	0.1039	709.8	0.17711	716.8	0.31103	723.8	0.02122
703	0.11422	710	0.17489	717	0.34729	724	0.02265
703.2	0.13655	710.2	0.17367	717.2	0.38966	724.2	0.02237
703.4	0.15183	710.4	0.18127	717.4	0.45263	724.4	0.02178
703.6	0.16947	710.6	0.18808	717.6	0.5264	724.6	0.02054
703.8	0.19434	710.8	0.19899	717.8	0.61496	724.8	0.02234
704	0.22979	711	0.20693	718	0.72037	725	0.03073
704.2	0.27844	711.2	0.23085	718.2	0.85828		
704.4	0.33091	711.4	0.26727	718.4	1.06376		
704.6	0.39738	711.6	0.32516	718.6	1.09732		
704.8	0.47344	711.8	0.3917	718.8	1.229		
705	0.54329	712	0.48696	719	1.2291		
705.2	0.65	712.2	0.55317	719.2	1.17712		
705.4	0.7179	712.4	0.68099	719.4	0.97044		
705.6	0.7939	712.6	0.86984	719.6	0.88007		
705.8	0.82	712.8	1.14007	719.8	0.71277		
706	0.81	713	1.2651	720	0.5983		
706.2	0.81402	713.2	1.33466	720.2	0.48499		
706.4	0.79331	713.4	1.39	720.4	0.38384		
706.6	0.7157	713.6	1.22307	720.6	0.29548		
706.8	0.704	713.8	0.93156	720.8	0.2312		

TABLE 2 The reduced absorption coefficient of the cesium diffuse band (in units 10^{-36} cm^5) as a function of wavelength

density. The results were compared with corresponding reduced absorption coefficient published some time ago [13]. The earlier measurements were performed in a cell equipped with sapphire windows with well defined length and without buffer gas. The cesium number density was determined by measuring the cell temperature and using the vapor pressure curve [6]. The reduced absorption coefficients in the line wing k/N^2 obtained in the present experiment are about 10% higher than those published in [13]. This means that the disagreement in the determination of Cs number density amounts to about 5%, which confirms the validity of the method presented here.

The investigated triplet bands are relatively narrow and spectrally well isolated. Therefore, we conclude that these bands can be used as very simple and accurate standards for the determination of the cesium atomic number density in the range from $5 \times 10^{16} \text{ cm}^{-3}$ to $5 \times 10^{18} \text{ cm}^{-3}$.

ACKNOWLEDGEMENTS The authors gratefully acknowledge financial support by the Ministry of Science, Education and Sports (Croatia), the Ministry of Innovation, Science, Research and Technology of the state

North Rhine-Westphalia and the Ministry of Education and Research of the Federal Republic of Germany.

REFERENCES

- 1 A. Thorne, U. Litzén, S. Johansson, *Spectrophysics* (Springer, Berlin, 1999)
- 2 V. Horvatic, R. Beuc, M. Movre, C. Vadla, *J. Phys. B* **26**, 3679 (1993)
- 3 D.E. Johnson, J.G. Eden, *J. Opt. Soc. Am. B* **2**, 721 (1984)
- 4 C. Vadla, R. Beuc, V. Horvatic, M. Movre, A. Quentmeier, K. Niemax, *Eur. Phys. J. D* **37**, 37 (2006)
- 5 V. Horvatic, M. Movre, C. Vadla, *J. Phys. B* **32**, 4957 (1999)
- 6 A.N. Nesmeyanov, *Vapor Pressure of the Chemical Elements* (Elsevier, Amsterdam, London, New York, 1963)
- 7 J. Szudy, W.E. Baylis, *Phys. Rep.* **266**, 127 (1996)
- 8 D.L. Drummond, L.A. Schlie, *J. Chem. Phys.* **65**, 2116 (1976)
- 9 R. Gupta, W. Happer, J. Wagner, E. Wennmyr, *J. Chem. Phys.* **68**, 799 (1978)
- 10 R. Beuc, H. Skenderovic, T. Ban, D. Veza, G. Pichler, W. Meyer, *Eur. Phys. J. D* **15**, 209 (2001)
- 11 C.M. Dion, O. Dulieu, D. Comparat, W. de Souza Melo, N. Vanhaecke, P. Pillet, R. Beuc, S. Milosevic, G. Pichler, *Eur. Phys. J. D* **18**, 365 (2002)
- 12 U. Diemer, J. Gress, W. Demtröder, *Chem. Phys. Lett.* **178**, 330 (1991)
- 13 H. Heinke, J. Lawrenz, K. Niemax, K.-H. Weber, *Z. Phys. A* **312**, 329 (1983)