

Pressure Broadening of the Cadmium 326.1 nm Line

G D Roston and M S Helmi

Department of Physics, Faculty of Science, Alexandria University,
P.O. Box 21511, Alexandria, Egypt

Dr.gamal_daniel@yahoo.com

Abstract. The temperature dependence of the Cd line absorption profile at 326.1nm perturbed by inert gases (Xe, Kr, Ar, Ne and He) has been carefully studied over a wide spectral range in both blue and red wings using a high-resolution double-beam spectrometer. The atomic densities of inert gases (N_{gas}) and cadmium (N_{Cd}) was sufficient to study the wing of the Cd line at 326.1nm. The temperature dependence of the studied line profile was analyzed in the framework of the quasi-static theory. The van der Waals coefficient differences (ΔC_6^0 and ΔC_6^1) between the ground $X0^+$ state and the two excited states A^30^+ and B^31 were obtained from the near red wing profile using Kuhn's law. All the results of the well depths with their positions for the ground ($X0^+$), and the excited ($^31, ^30^+$) were determined. The obtained results are compared with the corresponding theoretical and experimental molecular beam experiments results.

1. Introduction

The Cd – Cd and Cd – inert gas systems are considered to be a class of excimer molecules having shallow ground states and several much more strongly bound excited states. Recently, there have been numerous theoretical and experimental spectroscopic determinations of interatomic potentials for the ground X^10^+ and the two excited states A^30^+ and B^31 of these systems [1-38]. This paper is mainly devoted to obtain the interaction potentials of the ground state ($X0^+$) and both excited states A^30^+ and B^31 from the temperature dependence of the profile of Cd line 326.1 nm broadened by inert gases (Xe, Kr, Ar, Ne and He) pressure. These profiles are assigned to the transition ($A \rightarrow X0^+$ and $B \rightarrow X0^+$) this was illustrated in Refs. [1-7].

2. Theoretical aspects

2.1 The quasi-static theory

The Unified Frank-Condon (UFC) treatment of pressure broadening of spectral lines developed by Szudy and Baylis [39] reduces in the appropriate limits to the quasi-static theory in the far wings of the line. Using this theory, the reduced absorption coefficient ($K_n^m(\Delta\nu, T) \text{ cm}^5$) in the line wings as a consequence of two particle interactions normalized to the perturbing (N_{gas}) and the radiating (N_{cd}) atom densities is given by



$$K_n^m(\Delta\nu, T) = \frac{k^m(\Delta\nu, T)(\text{cm}^{-1})}{N_{Cd} N_{gas}} = 4\pi C_m R^2 \left| \frac{dR}{d(\Delta V_m)} \right| \exp \frac{-\nu_g(R)}{KT}, \quad (1)$$

where the symbol $m = 0$ and 1 are assigned to the 30 and 31 excited states respectively, R is the internuclear separation, $\Delta V_m(R)$ is the potential difference between the excited $V_m(R)$ and the ground $V_g(R)$ state potentials, given by $\Delta V_m(R) = V_m(R) - V_g(R) = h \Delta\nu$ and $\Delta\nu = \nu_0 - \nu$ is the frequency separation from the unperturbed line frequency ν_0 . C_m is the constant which relates the absorption coefficient to the normalized emission intensity. It is given by:

$$C_m = (\pi e^2 / m c) (g_m / g_j) f_{eg}$$

where e and m are the electron charge and mass, c is speed of light, g_j and g_m are the atomic and molecular statistical weights ($g_m = 1$ or 2 for $m = 0$ or 1) and f_{eg} is the oscillator strength for this atomic transition.

2.2 Determination of the van der Waals Coefficients.

The part of wings near to the line center is arising as a result of electronic transition between the states which are only slightly perturbed by the long-range van der Waals interactions of the form $\Delta V(R) = \Delta C_6 R^{-6}$. In this range of interaction, $V_g(R) \ll kT$, then Eq.(1) leads to Kuhn's law as:

$$K_n^m(\Delta\nu) = \frac{2\pi C_m}{3} h^{-3/2} (\Delta C_6^m)^{1/2} \Delta\nu^{-3/2} = A_m (\Delta\nu)^{-3/2} \quad (2)$$

If $\log K_n^m(\Delta\nu)$ is plotted versus $\log(\Delta\nu)$, a straight line results with a slope of $(-3/2)$. The ΔC_6^m constant may then be obtained from the calculation of the coefficient A_m . Generally for Cd – rare gases such a linear dependence on $\log K_n^m(\Delta\nu)$ is observed in two regions of the near red wing profile for more detailed see [2-6, 12].

2.3 Determination of potentials from line shape data

A more general method of inversion for the relation between the spectral line profile and $\Delta V_m(R)$ has been developed by Behmenburg [40] and Gallagher [41]. In this method the condition that $R(\Delta\nu)$ is a single-valued function and no overlapping bands ought to be fulfilled, then the spectral line profile can be interpreted in the framework of the quasi-static theory. From the temperature dependence spectra $K_n^m(\Delta\nu, T)$ of Eq.(1), it is possible to deduce both $V_g(R)$ and $\Delta V_m(R)$ and hence the excited state potentials from line shape data. The plot between $\log K_n^m(\Delta\nu, T)$ and $1000/T$ for a fixed $\Delta\nu$ gives a straight line. The slope of this plot gives $V_g(\Delta\nu)$ and extrapolation to the infinite temperature gives $K_n^m(\Delta\nu, T \rightarrow \infty)$. for more detailed see [2-6, 12].

3. Experimental aspects

The apparatus for this experiment is identical to that described elsewhere [1-8, 12]. A high pressure XBO 150 xenon lamp was used as a background source for absorption. In this case two identical absorption quartz cells were used, a sample cell filled with Cd + inert gas mixture and an empty reference cell. They were placed in a special double cell oven which could operate at a temperature up to 1300 K. The contributions due to the optical system were canceled in view of the double beam method being used. The atomic densities of inert gas N_{gas} and cadmium N_{Cd} were taken as those in [1-9]. The vapor pressures were calculated using Bousquet's formula [11].

4. Results and discussion

4.1 Blue wing profile of the Cd line 326.1 nm.

Due to large numbers of graphs of Cd – inert gases, sometimes the Cd – Ar graphs are presented as examples. Fig.(1) illustrates the experimental blue wing profile resulting from Cd – inert gases and the (Cd-Cd) interactions [1-8] at the same cadmium density. It is seen from this figure that the contributions from Cd-Cd is very small in the range of frequencies $20 \leq \Delta\nu \leq 200 \text{ cm}^{-1}$. For frequencies $\Delta\nu \geq 200 \text{ cm}^{-1}$ the absorption is mainly attributed to the Cd-Cd system. Consequently, the

absorption profile of the experimental Cd-inert gas was corrected for Cd-Cd contributions in the range of frequencies $20 \leq \Delta\nu \leq 200 \text{ cm}^{-1}$ and was tentatively analyzed for pure Cd-gas up to 200 cm^{-1} [2-8].

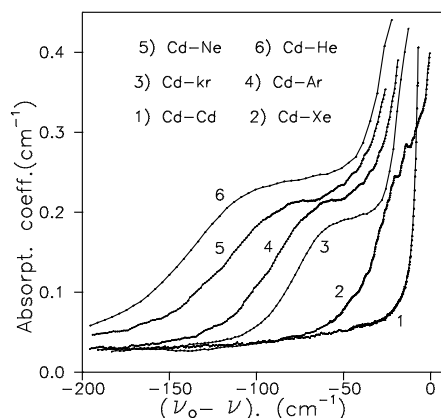


Figure 1: The experimental blue wing profile for pure Cd – Cd and Cd -inert gases interactions.

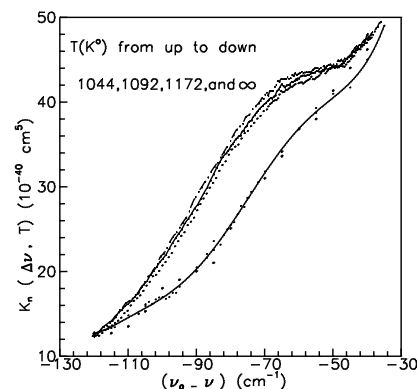


Figure 2: The temperature dependence for the blue wing of the pure Cd-Ar profile.

It is also seen from this figure that the profile has a quadratic form in the near wing which emphasizes that the profile is Lorentzian in this region. The existence of a broad maximum (blue satellite) is attributed to a maximum in the potential difference $\Delta V1 = V(B31) - V(X0+)$. The temperature dependence of the pure Cd-Ar profile (as an example of Cd-inert gases) is illustrated in Fig.(2). According to the UFC theory developed by Szudy and Baylis [39], the profile in the region of the satellite can be interpreted on the frame work of the quasi- static theory [Eq.(1)] if it is multiplied by $(T)/6$ [2-8]. It is seen from Fig. (2), that the ground state potential $V_g = 0$, is at the intersection point of the profiles ($\Delta\nu \approx 125 \text{ cm}^{-1}$) for Cd – Ar interaction.

Figure (3) shows the $\ln K_{mn}(\Delta\nu, T)$ values plotted against $1000/T$ for some values of $\Delta\nu$. Within the error bounds, the linear relation is well observed. The slopes of the calculated least- squares lines give the ground state potential $V_g(\Delta\nu)$ as a function of $\Delta\nu$. This is shown in Fig.(4). The infinite temperature intercepts determine the $K_{mn}(\Delta\nu, T \rightarrow \infty)$ values [see Fig.(2)].

The relation between $\Delta\nu1$ and the internuclear separation R can be obtained using the integration (6). For Cd-Ar, the starting point of this integration R_a was taken as the position of the ground state potential well depth deduced by [8] ($R_a = 4.3 \text{ \AA}$). The corresponding frequency separation, $\Delta\nu_a \approx 72 \text{ cm}^{-1}$, is taken from Fig.(4).

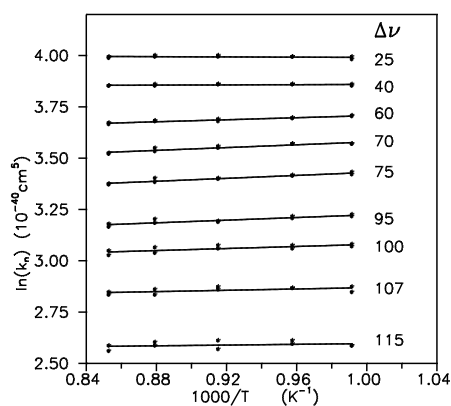


Fig. 3: The relation between the Cd-Ar blue wing profile $\ln k(\Delta\nu)$ against $1000/T$ for different values of $\Delta\nu$ (cm^{-1}).

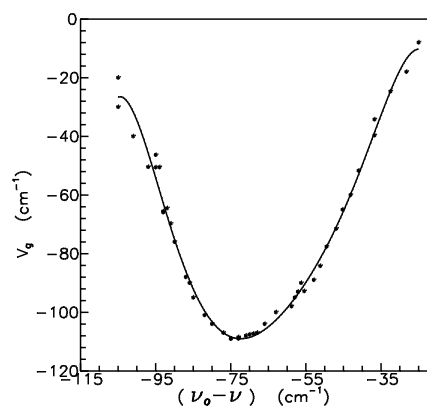


Fig. 4: The V_g potential plotted against $\Delta\nu$, experimental results(**) with its fitting curve (—).

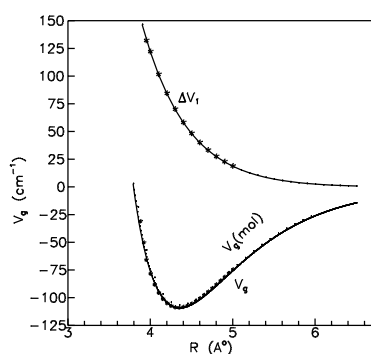


Figure 5: The ground state potential $V_g(R)$, and the potential difference $\Delta V_1(R)$ for cd-Ar system.

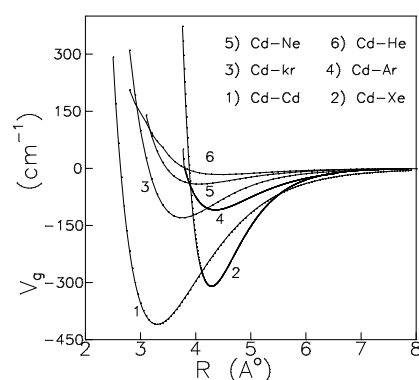


Figure 6: The ground state potential $V_g(R)$, for pure Cd – Cd and Cd inert gases system.

Using these values ($R_a = 4.3 \text{ Å}$, $\Delta v_a \approx 72 \text{ cm}^{-1}$) and the absorption profile at $T \rightarrow \infty$ (K_m^n (Δv , $T \rightarrow \infty$)) from Fig.(2), then the potential difference $\Delta V_1(R)$ can be obtained, then it is fitted to the polynomial function with a proper parameters as shown in Fig. (5). As $\Delta V_1(R)$ is obtained, the ground state V_g as a function the internuclear separation R can be recalculated, then $v_g(R)$ is fitted to the Morse potential as showing in Fig. (5). Then the potential curve of the excited state $V_1(R)$ [$V_1(R) = V_g(R) + \Delta V_1(R)$] can be calculated. Fig. (6, 7) shows ground $V_g(R)$ and the excited $V_1(R)$ states for pure Cd – Cd and Cd inert gases.

4.2 Red wing profile of the Cd line 326.1 nm.

The red wing profile of the Cd 326.1 nm line broadened by inert gases [2, 8], compared with the self broadened line profile obtained from [1], in logarithmic scale is illustrated in Fig.(8). In this figure one can see a single satellite at about 10 cm^{-1} . In the vicinity of this band two linear regions with slope ($-3/2$) are observed for the (Cd-gas) system. The first region lies between 2 and 10 cm^{-1} from the line center may be interpreted as the quasi-static line wing which is formed by transitions between the ground state 1^0+ and excited states 3^0+ as well as 3^1 , while the second region lies between 18 and 100 cm^{-1} is attributed to the transition between the ground X^10+ and the excited (3^0+) states only. The values of van der Waal's coefficient difference ΔC_6^0 and ΔC_6^1 for the two transition ($A^30+ \rightarrow X^10+$) and ($B^31 \rightarrow X^10+$) are obtained respectively. These results are illustrated in Table I.

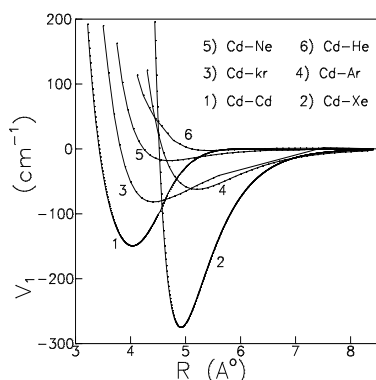


Figure 7: The excited state potential $V_1(R)$, for pure Cd – Cd and Cd inert gases.

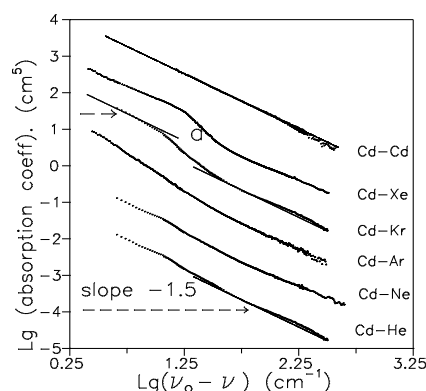


Figure 8: Red wing profiles for Cd-Cd and Cd-inert gases in logarithmic scale ($10\text{-}40 \text{ cm}^5$). The Cd-Xe, Cd-Kr, Cd-Ar, Cd-Ne and Cd-He profiles are divided by 10, 102, 103, 104, 105. respectively

Table 1. The van der Waals coefficients in eV Å⁶ for the Cd-inert gases system

Molecule	Cd – Cd	Cd - Xe	Cd – Kr	Cd - Ar	Cd - Ne	Cd - He
ΔC_6^0	-----	43.0 ± 3	37.8 ± 2	28.7 ± 2	23.5 ± 2	14.8 ± 2
ΔC_6^1	106.8 ± 2.3	86.0 ± 4	58.5 ± 3	48.0 ± 4	39.3 ± 3	28.5 ± 3

The potential $V_0(R)$ for the state ($^30^+$) can be obtained from the temperature dependence of the red wing profile. As the temperature dependence of this wing is very weak, then the ground state potential $V_g(R)$ can't be determined from the red wing profile. Nevertheless in this case the excited state potential $V_0(R)$ can be obtained with sufficient accuracy, if $V_g(R)$ is known from other data. By using the ground state potential $V_g(R)$ obtained from the blue wing and the red wing profile at any temperature T ($K_m^n(\Delta\nu, T)$), it was possible to obtain the potential difference $\Delta V_0(R)$ if the starting point $R_a(\Delta\nu_a)$ in the integration (8) is established. This point was obtained due to the fact that Kuhn's law is observed in the near red wing at $20 < \Delta\nu < 100 \text{ cm}^{-1}$ and the van der Waals potential difference $\Delta V_a = \Delta C_6^0 R_a^{-6}$ can be applied. $\Delta V_0(R)$ with the used ground state are presented in Fig.(9). Fig. (10) shows the determined $V_0(R)$ for pure Cd – Cd and Cd -inert gases interactions.

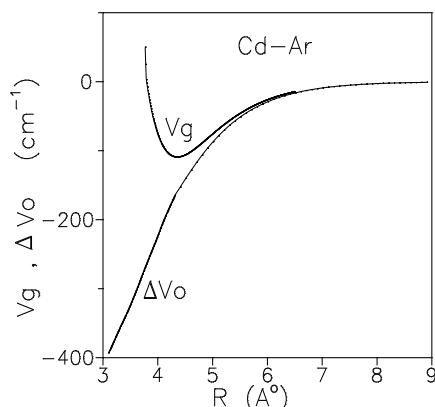


Figure 9: The ground state potential $V_g(R)$, and the potential difference $\Delta V_0(R)$ for Cd-Ar.

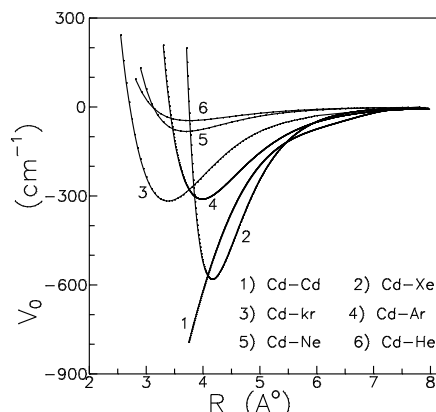


Figure10: The excited state potential $V_0(R)$, for pure Cd – Cd and Cd inert gases.

The potential parameters, well depth ϵ (cm^{-1}) and its positions R (\AA) of the ground X^10^+ and the two excited 31 and $^30^+$ states for pure Cd - Cd and Cd – Inert gases (Xe, Kr, Ar, Ne and He) are illustrated in tables II and III.

Table II: Comparison of our data for the ground X^10^+ and the two excited states $A^30_u^+$ and B^31_u potentials parameters (ϵ (cm^{-1}), R (\AA)) for pure Cd – Cd.

Molecule	$X^10_g^+$		$A^30_u^+$		B^31_u		Ref.
	ϵ_g (cm^{-1})	R_g (\AA)	ϵ_0 (cm^{-1})	R_0 (\AA)	ϵ_1 (cm^{-1})	R_1 (\AA)	
Cd-Cd	386 ± 27	3.3 ± 0.1	293 ± 18	3.5	>1400	≤ 3	1
	386 ± 27	4.82	290 ± 18	4.95	-	-	1,8
	410 ± 30	3.3 ± 0.1	-	-	-	-	11
	380	4.82	-	-	-	-	12
	150	4.76	-	-	5650	-	13
	323	4.26	252	4.52	-	-	14
	-	-	235	-	≥ 315	-	15
	328 ± 3	3.76, 3.78	259.9 ± 2.9	4.02 ± 0.03	-	-	16,17

Table III: Comparison of our data for the ground X^{10+} and the two excited states A^{30+} and B^31 potentials parameters (ϵ (cm⁻¹), R (Å)) for Cd – inert gases.

Molecule	X^{01+}		A^{30+}		B^{31}		Ref.
	ϵ_g (cm ⁻¹)	R_g (Å)	ϵ_0 (cm ⁻¹)	R_0 (Å)	ϵ_1 (cm ⁻¹)	R_1 (Å)	
Cd-Xe	192±18	4.28	988±41	3.93	152±15	4.41	2
	230.4	4.28	-	-	-	-	9
	370	4.73	-	-	-	-	18
	185	-	-	-	-	-	19
	-	-	1086±60	-	-	-	20
	198	4.45	-	-	677±4	4.26±0.05	21,22
Cd-Kr	134±7	3.99	389±10	3.25	73±4	4.45	3, 8
	130	3.75	-	-	-	-	11
	-	-	-	-	109.7	4.73	22
	131	-	373	-	72	-	23
	114.5	4.5	498.9	3.5	60.2	5.07	24
	310	3.63	407.2	3.44	-	3.5	18
	165, 129	4.27	-	-	-	-	25,19
	-	-	555.0 ± 0.5	3.3 ± 0.03	-	-	26
Cd-Ar	109.7±3	4.3	310.315	3.95	63.2±2	4.77±0.15	4, 8
	-	-	326	3.38	-	-	18
	-	-	325	3.45	-	-	20
	-	-	-	-	55.0±0.8	5.01±0.05	22,23
	106.5	4.3	-	-	59.7	5.03±0.03	24
	106	4.31	322	3.5	56	-	28
	106.8	4.31	314.9 ± 6.1	3.51±0.03	57.0 ± 2.9	5.07 ± 0.03	29,26
	112	4.29	-	-	-	-	30
Cd-Ne	106.7	4.31	-	-	-	-	31
	41.4±3	4.37±0.2	82.5±4	3.7±0.2	18.03±2	4.25±0.3	6, 8
	-	-	-	-	5.01±0.05	5.29±0.05	22
	39	-	75	-	21	-	24
	38	4.1±0.2	90.6	3.1±0.2	19.3	4.8	28
	-	4.26	-	3.62±0.05	-	-	20
	27	4.28	75	3.61	19.3	4.96	32
Cd-He	28.3	4.32	70.5	-	19.6	4.98	33,34
	16.3±2	4.5±0.2	45.8±4	3.8±0.2	2.55±0.5	4.94±0.3	7,8, 9
	-	-	-	-	7.8±0.2	7.8±0.2	22
	14.2	4.42	41.2	2.92	6.1	4.54	35
	-	-	-	-	2.5	5.715	36
	14.2	4.6	41.2	3.7	6.1	4.8	37
	15.1	4.5	36	3.57	7.8	5.55	30
	16.8	4.2	27.5	3.57	-	-	38

It is seen from Tables II and III, that the obtained potential parameters of the ground X^{10+} and the two excited states $^{30+}$ and 31 are in good agreement with the corresponding theoretical and experimental molecular beams.

References

- [1] Helmi MS, Grycuk T, Roston GD 1996 *Spectrochim. Acta B* **51** 633
- [2] Helmi MS, Grycuk T, Roston GD 1996 *Chem. Phys.* **209** 53
- [3] Roston GD, Ghatass ZF 2008 *J. Quant. Spectrosc. Radiat. Transf.* **109** 2427
- [4] Roston GD, Grycuk T, Helmi MS 1996 *Chem. Phys.* **213** 365
- [5] Roston GD, Helmi MS 2000 *Chem. Phys.* **258** 55
- [6] Roston GD 2004 *J. Quant. Spectrosc. Radiat. Transf.* **87** 83
- [7] Roston GD 2005 *Phys. Scr.* **72** 31
- [8] Roston GD, Helmi MS 2006 *J. Quant. Spectrosc. Radiat. Transf.* **101** 201
- [9] Roston GD, Ghatass ZF 2006 *J. Quant. Spectrosc. Radiat. Transf.* **101** 205
- [10] Roston G.D, Helmi MS 2009 *J. Chem. Phys.* **358** 30
- [11] Bousquet C 1986 *J. Phys. B: At. Mol. Phys.* **19** 3859
- [12] Roston GD, Helmi MS 2014 *J. Quant. Spectrosc. Radiat. Transf.* **140** 30
- [13] Bender CF, Rescigno TN, Schaefer H F, Orel AH 1979 *J. Chem. Phys.* **71** 1122
- [14] Czajkowski M, Bobkowski R, Krause L 1989 *Phys. Rev.* **40** 4338
- [15] Kowalski A, Czajkowski M, Breckenridge WH 1985 *Chem. Phys. Lett.* **119** 368
- [16] Strojecki M, Ruszczak M, Łukomski M, Koperski J 2007 *Chem. Phys.* **340** 171
- [17] Strojecki M, Krośnicki M, Zgoda P, Koperski J 2010 *Chem. Phys. Lett.* **489** 20
- [18] Czuchaj E, Sienkiewicz J 1984 *J. Phys. B* **17** 2251
- [19] Funk J D, Breckenridge WH *J. Chem. Phys.* **90** 2927
- [20] Kvaran A, Funk D J, Kowalski A, Breckenridge WH 1988 *Chem. Phys.* **89** 6069
- [21] Strojecki M, Krośnicki M, Łukomski M, Koperski J 2009 *Chem. Phys. Lett.* **471** 29
- [22] Koperski J, Urbanczyk T, Krośnicki M, Strojecki M 2014 *Chem. Phys.* **428** 43
- [23] Urbanczyk T, Koperski J 2014 *Chem. Phys. Lett.* **591** 64
- [24] Kowalski A, Czajkowski M, Breckenridge W H 1985 *Chem. Phys. Lett.* **121** 217
- [25] Czajkowski M, Bobkowski R, Krause L 1991 *Phys. Rev. A* **44** 5730
- [26] Urbanczyk T, Strojecki M, Koperski J 2011 *Chem. Phys. Lett.* **503** 18
- [27] Koperski J, Łukomski M, Czajkowski M 2002 *Spectrochim. Acta Part A* **58** 2709
- [28] Bobkowski R, Czajkowski M, and Krause L 1990 *Phys. Rev A* **41** 234
- [29] Koperski J, Kielbasa M, Czajkowski M 2000 *Spectrochim. Acta Part A* **56** 1613
- [30] Czuchaj E, Stoll H 1999 *Chem. Phys.* **248** 1
- [31] Koperski J, Czajkowski M 2002 *J. Mol. Spectrosc.* **212** 162
- [32] Czajkowski M, Krause L, Bobkowski R 1994 *Phys. Rev A* **49** 775
- [33] Strojecki M, Krośnicki M, Koperski J 2009 *J. Mol. Spectrosc.* **256** 128
- [34] Koperski J, Czajkowski M 2000 *Eur. Phys. J. D* **10** 363
- [35] Koperski J, Czajkowski M 1998 *J. Chem. Phys.* **109** 459
- [36] Zagrebin A L, Lendnev M G 1993 *Opt. Spectrosc.* **75** 562
- [37] Koperski J, Czajkowski M A 2001 *Chem. Phys. Lett.* **350** 367
- [38] Czuchaj E, Krośnicki M, Stoll H 2001 *Theor. Chem. Acc.* **105** 219
- [39] Szudy J, Baylis W 1975 *J. Quant. Spectrosc. Radiat. Transf.* **15** 641
- [40] Behmenburg W 1972 *Z. Naturforsch.* **27a** 31
- [41] Gallagher A 1975 *Atomic Physics*, vol. 4 (New York and London: Plenum)