SPECTROSCOPIC CHARACTERISATION OF THE $X0^+$, $A0^+$ AND $B1$ MOLECULAR STATES OF THE CdXe VAN DER WAALS COMPLEX*

J. Koperski, M. Łukomski

M. Smoluchowski Institute of Physics, Jagellonian University
Reymonta 4, 30-059 Kraków, Poland
`ufkopers@cyf-kr.edu.pl`
`lukomski@castor.if.uj.edu.pl`

and M. Czajkowski

Department of Physics, University of Windsor
Windsor, Ontario, N9B 3P4, Canada
`mczajko@server.uwindsor.ca`

(Received June 11, 2002)

An excitation spectrum of the $B1 \leftarrow X0^+$ transition in CdXe has been recorded in a supersonic beam crossed with a pulsed dye laser beam. A thorough analysis of the data yielded the bond strength $D'_e = (227.9 \pm 5.0)\,\mathrm{cm}^{-1}$, fundamental frequency $\omega'_e = (18.3 \pm 0.3)\,\mathrm{cm}^{-1}$, anharmonicity $\omega'_e x'_e = 0.37\,\mathrm{cm}^{-1}$, and internuclear equilibrium separation $R'_e = (4.26 \pm 0.05)$ Å in the excited $B1(5^3P_1)$ state of the molecule. Molecular spectroscopic constants of the $X0^+(5^1S_0)$ ground state were also determined from the experimental data: $D''_e = (276.0 \pm 5.0)\,\mathrm{cm}^{-1}$, $\omega''_e = (33.1 \pm 0.6)\,\mathrm{cm}^{-1}$, $\omega''_e x''_e = (0.99 \pm 0.02)\,\mathrm{cm}^{-1}$, and $R''_e = (4.21 \pm 0.05)$ Å. The ground-state results were obtained from a direct observation of various "hot" bands in the $B1 \leftarrow X0^+$ transition. A repeat of earlier work of Funk and Breckenridge *J. Chem. Phys.* **90**, 2927 (1989), and Helmi *et al., Chem. Phys.* **209**, 53 (1996), relating to the $A0^+ \leftarrow X0^+$ transition yielded improved results which were essential for the correct spectroscopic characterisation of the $A0^+(5^3P_1)$ state of the molecule.

PACS numbers: 33.20.Lg, 33.20.Tp, 33.15.Fm

---

* Presented at the Photons, Atoms and All That, PAAT 2002 Conference, Cracow Poland, May 31–June 1, 2002.

1. Introduction

Among numerous articles on the formation and spectroscopic characterisation of CdRG (RG — Rare Gas) van der Waals (vdW) molecules which appeared over the last decade, there are only two reports related to the CdXe complex studied in a free supersonic jet crossed with a laser beam [1, 2]. An explanation for the paucity of studies on this molecule may be that whilst lighter rare gases (He, Ne or Ar) used as carriers in the jet expansion techniques are relatively inexpensive, the heavier ones (Kr, Xe) are very expensive, dramatically increasing experimental cost. The situation is even worse for the CdXe complex, which can only be produced (for experimental reasons) in a continuous supersonic beam and with a relatively large consumption of the carrier gas. Without a proper description of the heaviest molecule our knowledge about these weakly bound complexes is incomplete and a reliable formulation of a general theoretical description of the whole CdRG family is difficult. Generally, all what is available on the subject in the literature are early articles of Kvaran *et al.* [1], Funk and Breckenridge [2], and recent paper of Helmi *et al.* [3] with an essentially different experimental approach. Kvaran *et al.* [1] recorded the vibrational excitation spectrum of the $A0^+ \leftarrow X0^+$ transition (shown schematically in Fig. 1) and using a Birge–Sponer (B–S) analysis deduced spectroscopic constants related to the excited $A0^+(5^3P_1)$ state. No information was available on the ground $X0^+(5^1S_0)$ nor on the other excited $B1(5^3P_1)$ state. Funk and Breckenridge [2] investigated two excited states $C^1\Pi_1$ and $D^1\Sigma_0^+$ correlated to the 5^1P_1 Cd-atomic asymptote, and from the "action spectrum" for excitation of the $D^1\Sigma_0^+$ state the ground-state dissociation energy was evaluated to be $D_0'' = 176 \pm 5\,\mathrm{cm}^{-1}$. Helmi *et al.* [3] studied the temperature dependence of the absorption profile of the Cd 326.1 nm line perturbed by Xe collisions. The experiment was performed in a fluorescence cell and values of dissociation energies of particular molecular states were obtained *indirectly,* in a not convincing way and are, therefore, suspect. It is expected that the $B1$ excited state in the CdXe complex should be possible to observe as it is in fact in the CdHe [4], CdNe [5, 6], CdAr [5, 7], and CdKr [5, 8, 9] molecules. From our experience, the $B1 \leftarrow X0^+$ transition is difficult to produce using experimental conditions, which are suitable for the $A0^+ \leftarrow X0^+$ absorption reported in Ref. [1] (*i.e.*, 1% Xe admixture with Ar). A knowledge on the $B1 \leftarrow X0^+$ transition is of great importance. Both $A0^+$ and $B1$ molecular states asymptotically converge to the same 5^3P_1 Cd-atomic asymptote. Dissociation energies (*i.e.*, $D_0'(A0^+)$ and $D_0'(B1)$) combined with the $\nu_{00}(v' = 0 \leftarrow v'' = 0)$ and E_{at} energies (see Fig. 1) yield the ground state dissociation energy D_0''. The value of the latter must be the same as values deduced from both spectra separately. Therefore, we have a sensitive

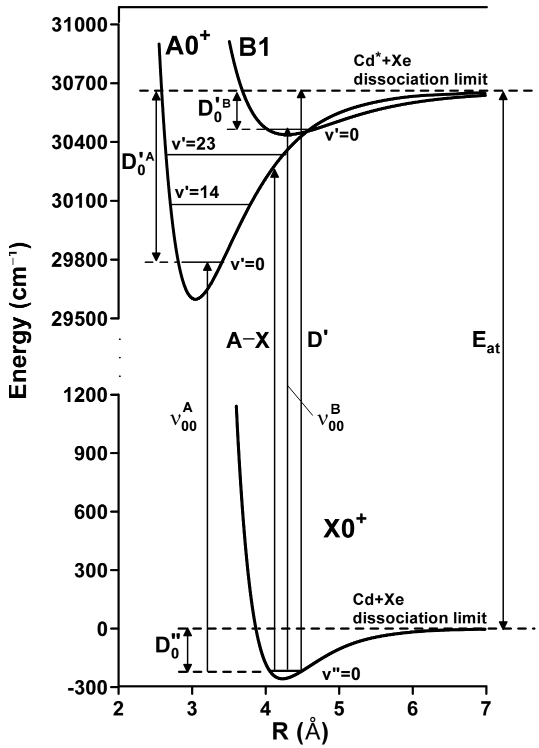

Fig. 1. Potential energy curves for CdXe molecule and transitions involved in the experiment. All potentials are represented by Morse functions. The $A0^+ \leftarrow X0^+$ transition, ν_{00} transitions as well as dissociation energies and D' dissociation limit are depicted.

tool for verification of the spectroscopic constants of both excited states. These can be obtained *independently* from the excited-state characteristics once *direct* experimental information on the ground state is available [8]. In Ref. [8] a different than in Ref. [1] value of D_e'' was predicted and eventually it generated the $D_e'(B1)$. However, all of this was based on semi-empirical speculations with little experimental merit.

In this report, we present for the first time results of experimental studies on the $B1 \leftarrow X0^+$ transition in CdXe complex formed in a supersonic continuous beams. We observed not only the excitation spectrum mentioned above, but we have also created favourable conditions [10] for the formation of "hot" bands providing valuable information on the energy structure of the CdXe ground state. Hence, we report the reliable spectroscopical characterisation of the ground $X0^+$ and excited $B1$ states. Finally, we present a corrected set of spectroscopic constants for the $A0^+$ state showing the relationships between both excited and ground states.

2. Experimental

The arrangement of apparatus and details of measurements were described previously [4, 7, 9]. The experiment was performed *independently* in two laboratories (in Windsor [4, 9] and in Kraków [7, 9]) on similar experimental setups. Here, we present only these characteristics that differ the two arrangements (in square brackets those related to the experiment in Kraków). The Laser Induced Fluorescence (LIF) was observed in an evacuated expansion chamber into which the CdXe molecules, seeded in a gas mixture of 10 % Xe in pure Ne (research grade, Linde) [10 % Xe in pure He (Linde Gaz Polska)] were injected through a nozzle of $D = 150\,\mu$m [115 μm] in diameter. The nozzle was a part of a molecular beam source made of solid molybdenum. The molybdenum was chosen in spite of the fact that it is very difficult to machine because it has superior qualities at high temperatures. The surface of molybdenum is in contact with metallic Cd or Zn at high temperatures ($\approx$ of 1000 K) but is chemically inactive. By comparison, a stainless steel source begins to corrode soon after the oven reaches approximately 750 K and the nozzle is severely damaged and eventually clogged by the metal sample, whereas the molybdenum source keeps the nozzle clear for many hours and the source can be recharged many times.

The CdXe molecules in the beam were irradiated with a second harmonic output (KDP-C doubling crystal) of an in-house-built [Sopra, commercial] dye laser utilising a 6.0×10^{-4} Mℓ^{-1} [8.7×10^{-4} Mℓ^{-1}] solution of DCM in a dimethyl sulphoxide [methanol]. The dye laser was pumped with a second harmonic output from the Nd:YAG laser. The dye laser and the crystal were synchronously scanned over the range from 3250 Å to 3262 Å and from 3261 Å to 3300 Å in case of the $B1 \leftarrow X0^+$ and $A0^+ \leftarrow X0^+$ transitions, respectively. The wavelength calibration of the dye laser was frequently verified against a Fizeau [WA 4500 Burleigh] wavemeter and the spectral linewidth of 1/3 cm^{-1} [1/4 cm^{-1}] was determined by monitoring the fundamental frequency of the dye laser output with a Fabry–Perot etalon.

The resulting excitation spectrum was recorded at right angles to the plane containing the crossed molecular and laser beams and it was detected using a Schlumberger EMR-541-N-03-14 [Electron Tubes 9893QB/350] photomultiplier tube (PMT) with a photocathode which has maximum sensitivity in the UV and blue spectral regions. Additionally, in Windsor a narrow-band filter with $\Delta\lambda = 100$ Å FWHM centred at $\lambda = 3260$ Å was placed in front of the PMT to reject stray light and hence to improve the signal-to-noise ratio. The PMT signal was recorded with a Hewlett–Packard transient digitiser, model HP 54510 [Tektronix TDS-210] digitising scope and stored in a PC computer.

The beam source was operated at low pressure of about 10 torr inside the chamber. The carrier gas backing pressure, P_0, was maintained in the range of 6 to 7 atm, which is lower than usual (*e.g.* [4]). The reason for this is that when observing the excitation spectrum of the $B1 \leftarrow X0^+$ transition, we were aware of the fact that traces of the signal from the $0_u^+(^3\Pi_u) \leftarrow X0_g^+(^1\Sigma_g^+)$ transition of Cd_2 [11] may appear as unwanted bands in our spectrum of CdXe. Hence, we kept the temperature low, below the threshold of Cd_2 spectral visibility. Similarly, we were very cautious in not using a high pressure of the carrier gas which could introduce unwanted bands of the $B1 \leftarrow X0^+$ transition in the CdNe [6] [CdHe [4]] molecule. Thus, we could be certain that the formation of CdNe [CdHe] and Cd_2 molecules is at low and insignificant rate. We also took the extra precaution of running the experiment in the spectral region corresponding to the $B1 \leftarrow X0^+$ transition in CdXe with pure Ne [He] as the carrier gas and, therefore, did not observe any significant signal which may "contaminate" the CdXe spectrum. In order to detect transitions from vibrational levels higher than $v'' = 0$, we varied the X/D parameter from 15 to about 40 [from 26 to 61]. This caused a change of the excitation distance X, measured from the nozzle to the focused laser beam region, from 2 mm to 6 mm [from 3 mm to 7 mm]. Such changes in the distance X permitted observations of the LIF in different regions of the supersonic beam [10], corresponding to different conditions of temperature and an appropriate number of collisions between CdXe molecule and the carrier gas atoms. As a result, we observed "hot" vibrational bands originating from $v'' = 0$, 1, 2, 3 in the $B1 \leftarrow X0^+$ transition. In order to record a meaningful excitation spectrum for the $B1$ state we needed to average several laser-frequency scans of the corresponding spectral region because the signal was very weak. We considered it necessary to repeat the excitation spectrum of the $A0^+ \leftarrow X0^+$ transition in CdXe reported earlier in Ref. [1] and this was done using a less expensive mixture of the carrier gas, *i.e.*, 1 % Xe in pure Ne (Linde) [5 % Xe in pure He (Linde Gaz Polska)]. In this experiment we had to use higher P_0 backing pressure. For all experiments carried out, the mechanical and thermal stability of our apparatus and the reproducibility of the spectra were satisfactory.

3. Results and discussion

3.1. Excitation spectrum of the $B1(5^3P_1) \leftarrow X0^+(5^1S_0)$ transition

Fig. 2(a) shows the excitation spectrum of the $B1 \leftarrow X0^+$ transition in CdXe molecule recorded using 10 % Xe in Ne as a carrier gas. It should be stressed that an almost identical spectrum was recorded using 10 % Xe in He. The spectrum spans the wavelength region from $\lambda = 3254.5$ Å up to about $\lambda = 3262$ Å (*i.e.*, to the Cd-atomic resonance transition), and it

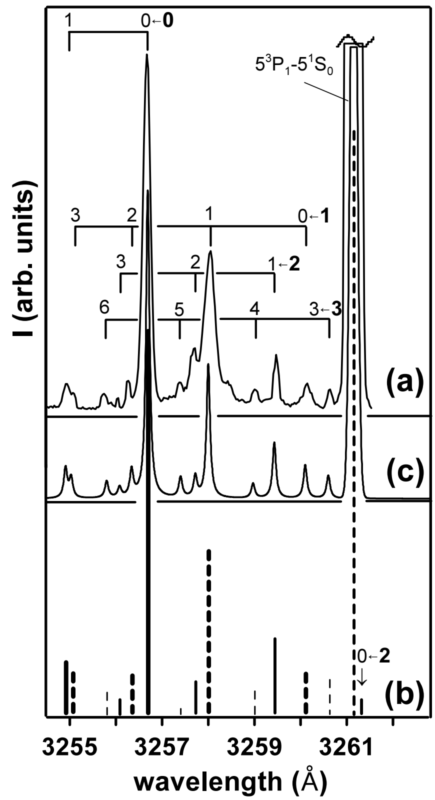

Fig. 2. Excitation spectrum of the $B1^+ \leftarrow X0^+$ transition in CdXe. 10% Xe in pure Ne mixture used as a carrier gas. (a) Experimental trace, $X = 6\,\mathrm{mm}$, $P_0 = 7\,\mathrm{atm}$. (b) Theoretical simulation of the spectrum (F–C factors). (c) Theoretical simulation of the total experimental spectrum, Lorentzian of 0.6 cm^{-1} (FWHM) was used for the laser convolution function, and Morse functions were assumed to represent the excited and the ground states. T_{vib}=70 K. The same spectrum was obtained with 10% Xe in pure He mixture used as a carrier gas.

shows two pronounced vibrational bands together with a total of eleven bands of much weaker intensity. All vibrational-band frequencies are listed in Table I. The spectrum is an average of 8 consecutive scans because in a single scan we observed the two strongest bands only. Because of the poor signal-to-noise ratio we were not able to record a fluorescence spectrum of either of these bands and, therefore, an identification of their v'-values based on a Condon Internal Diffraction (CID) pattern was not possible. We obtained the v'-assignment of recorded bands by a careful simulation procedure based on calculation of Franck–Condon (F–C) factors. The result is shown in Fig. 2(b) in the form of vertical bars. The height of the bars represents

TABLE I

Vibrational components of the $B1 \leftarrow X0^+$ transition in CdXe molecule.
[λ and ν are stated in air and vacuum, respectively]

$v' \leftarrow v''$	λ [Å]	ν [cm^{-1}]
0←0	3256.69	30696.8
1←0	3254.82	30714.4
0←1	3259.99	30665.7
1←1	3258.13	30683.3
2←1	3256.34	30700.1
3←1	3254.63	30716.3
1←2	3261.22	30654.2
2←2	3259.43	30671.0
3←2	3257.72	30687.1
4←2	3256.09	30702.5
3←3	3260.60	30660.0
4←3	3258.97	30675.4
5←3	3257.41	30690.0
6←3	3255.94	30703.9

an intensity of the corresponding transition, therefore, in the case of "hot" bands they carry information about a vibrational temperature, T_{vib}, of the molecule. We found that T_{vib}=70 K is consistent with the observed intensity ratios. Fig. 2(c) shows a simulation of the total spectrum assuming a realistic excitation linewidth and profile. The estimated linewidth of the excitation laser was less than 1cm^{-1}, and a Lorentzian line profile was assumed. The simulation indicates some overlapping of closely located bands and their possible deformation in shape and position of peak intensity. The calculation of the F–C factors was performed under the assumption that both (ground and excited) potential energy curves of the CdXe molecule are represented by a Morse potential with parameters obtained in this investigation (see Table IV). Therefore, the simulation procedure generated an additional parameter (related to the Morse potential), *i.e.*, a difference between the equilibrium internuclear separations $\Delta R_e = R_e'(B1) - R_e''$ of the corresponding molecular states. From the best simulation we obtained the value of $\Delta R_e = (0.05 \pm 0.01)$ Å. This relatively small value of ΔR_e agrees with our observed spectrum characterised by a relatively high intensity of the $v' = 0 \leftarrow v'' = 0$ transition and a rapid decrease of the F–C factors for higher v' levels. A spectrum with similarly small $\Delta R_e = 0.02\,\text{Å}$ and comparable features, though more pronounced than presented here, has previously been reported [12, 13].

3.2. The $v'' = 0$-progression of the $B1 \leftarrow X0^+$ transition

3.2.1. Birge–Sponer plot

The analysis of data from Table I leads to vibrational-energy components, which define the various v''-progressions in the $B1 \leftarrow X0^+$ transition. All components of the $v'' = 0$-progression can be deduced from the spectrum and Table I. The $v' = 0 \leftarrow v'' = 0$ and $v' = 1 \leftarrow v'' = 0$ components have been obtained directly from the experimental traces, while the next (*i.e.* $v' = 2 \leftarrow v'' = 0$) and the following (*i.e.* $v' = 3, 4, 5, 6 \leftarrow v'' = 0$) components have been extracted from the various "hot" bands observed in the experiment. For example the $v' = 2 \leftarrow v'' = 0$ component has been derived by taking the difference $\Delta G_{v'} = \nu_2(v' = 2 \leftarrow v'' = 1) - \nu_1(v' = 1 \leftarrow v'' = 1)$ and adding it to the proceeding frequency of the $v' = 1 \leftarrow v'' = 0$ band. Next, the $v' = 3 \leftarrow v'' = 0$ component has been obtained by adding the $\Delta G_{v'} = \nu_3(v' = 3 \leftarrow v'' = 1) - \nu_2(v' = 2 \leftarrow v'' = 1)$ to the frequency of the $v' = 2 \leftarrow v'' = 0$ band, *etc.* Using the B–S analysis we obtained a linear dependence of the $\Delta G_{v'+1/2}$ as a function of $v' + 1/2$ (see Fig. 3(a)). From the graph we obtained the fundamental frequency $\omega_0' = (18.0 \pm 0.2)\,\text{cm}^{-1}$ (short extrapolation), anharmonicity $\omega_0' x_0' = (0.37 \pm 0.01)\,\text{cm}^{-1}$ (slope), the value of $v_D' = 24.3$ at the dissociation limit (long extrapolation), and the dissociation energy $D_0' = (218.9 \pm 5.0)\,\text{cm}^{-1}$. Using $\nu_{00}(B1) = 30696.8$ cm^{-1} as the frequency of $v' = 0 \leftarrow v'' = 0$ transition from Table I, $E_{\text{at}}(5^3P_1) = 30656.0\,\text{cm}^{-1}$ [14] as the energy of the atomic transition in Cd, and the relationship

$$D_0'' + E_{\text{at}}(5^3P_1) = \nu_{00}(B1) + D_0'(B1) \tag{1}$$

we obtained a value of the ground-state dissociation energy of CdXe molecule, $D_0'' = (259.7 \pm 5.0)\,\text{cm}^{-1}$. Our result differs significantly from those reported in Refs. [2] and [3] (see Table IV below). We discuss these differences in Section 3.5.

3.2.2. LeRoy–Bernstein method

It is well known that weakly bound vdW complexes may frequently depart from being represented by a simple Morse potential leading to a failure (or serious errors) when using only the B–S method in order to obtain spectroscopic parameters from experimental data. This departure from a Morse

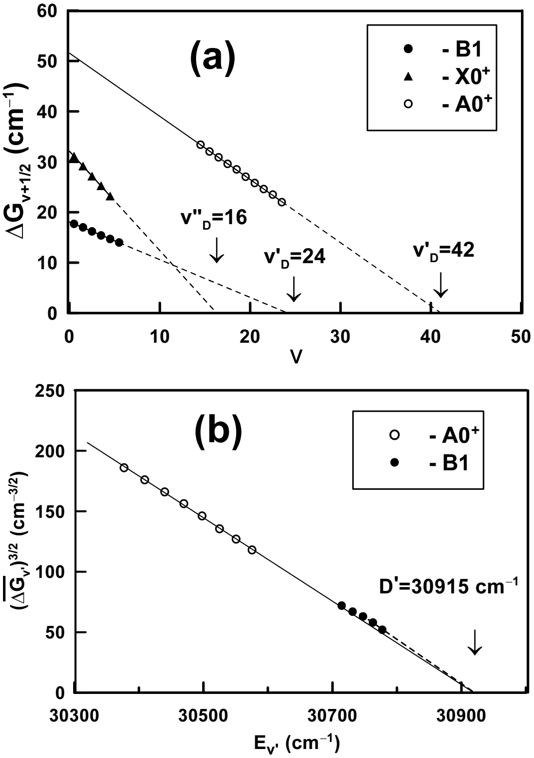

Fig. 3. (a) Birge–Sponer plots for the: $B1$ (filled circles), $X0^+$ (filled triangles), and $A0^+$ (open circles) states of CdXe. (b) LeRoy–Bernstein plot for the: $B1$ (filled circles), and $A0^+$ (open circles) states of CdXe.

representation is usually manifested by a significant error in evaluation of the dissociation energy of the molecule. The long-range part of a Morse potential ($R \gg R_e$) does not describe properly the dissociation energy of the molecule. As a rule, the dissociation energies (if different from the "true" bond strength) are always larger than the value of D_e measured and evaluated by means of the linear B–S method. Consequently, a Morse function cannot represent correctly dispersive (attractive) forces near the dissociation limit. These forces may provide a substantial contribution to the total bonding. The long-range behaviour of the $B1$-state PE curve can be approximated by an expression $U'_B(R) = D' - \sum_n C_n R^{-n}$, where D' is a dissociation energy of the $B1$ state (here, with respect to $v'' = 0$), C_n are constants, and n are determined by the nature of the long range attractive interaction between atomic partners in the complex. In the case of $B1$ state of the CdXe we can assume that an interaction of the primary importance is that of an induced dipole-induced dipole type [6, 7, 9]. It leads to $n = 6$ [15, 16].

Therefore, we approximated the long-range part of the $U'_B(R)$ potential by the C_6R^{-6} *leading term* and we employed a limiting LeRoy–Bernstein (LR–B) method [15] to analyse our results. According to the LR–B theory, the vibrational first differences

$$\Delta G_{v'}^{2n/n+2} = K_n^{2n/n+2}(D' - E_{v'})\,, \tag{2}$$

where constant K_n is defined as $K_n = [\hbar n\Gamma(1+1/n)]/[\mu C_n \Gamma(1/2+1/n)]$, μ is a reduced mass of CdXe, and Γ is a gamma function. Fig. 3(b) presents the LR–B (*i.e.*, $\Delta G_{v'}^{3/2}$ *versus* $E_{v'}$) plot for the $B1$ state. The plot determines the $B1$-state dissociation limit (intercept with the $E_{v'}$ axis). The value obtained is $D' = 30915 \pm 5\,\mathrm{cm}^{-1}$, and it is in a good agreement with our B–S estimation. However, we stress that this should only be treated as a result which *is not in contradiction* to the B–S extrapolation. The small number of contributing vibrational levels makes the results of the analysis uncertain [15].

3.3. Spectroscopic characterisation of the CdXe ground state

The $v'' = 0, 1, 2, 3$ vibrational components of the $X0^+$ state of the CdXe molecule have been extracted from the *experimentally* found "hot" bands in the $B1 \leftarrow X0^+$ transition (see Table I) giving three $\Delta G_{v''+1/2}$ values (*i.e.* $\Delta G_{1/2}$, $\Delta G_{3/2}$ and $\Delta G_{5/2}$). An additional two values of $\Delta G_{v''+1/2}$ (*i.e.* $\Delta G_{7/2}$, $\Delta G_{9/2}$) were *calculated* within an anharmonic oscillator approximation to show the correlation between the experimental and calculated differences (calculated values were based on ω''_e and $\omega''_e x''_e$ obtained from the experiment: $\omega''_e - 2\omega''_e x''_e(v''+1)$). The plot of $\Delta G_{v''+1/2}$ *versus* $v'' + 1/2$ is presented in Fig. 3(a) and shows an exact linear dependence. The plot defines well the ground-state fundamental frequency ω''_0 and anharmonicity $\omega''_0 x''_0$, and the relationship $\omega''_0/2\omega''_0 x''_0$ gives the quantum number v''_D for which $\Delta G = 0$. The area under the graph can be evaluated and it yields the dissociation energy $\mathrm{D}''_0 = 259.7\,\mathrm{cm}^{-1}$. The obtained value coincides exactly with that derived using the elementary summation expressed by Eq. (1) discussed above. To our knowledge, this is the first time that the ground-state spectroscopical constants of CdRG molecule have been obtained directly from experimental data by means of the B–S method. Usually the ground-state spectroscopic characterisation for this family of molecules is derived indirectly using Eq. (1) only, and employing additional assumptions on either the fundamental frequency ω''_e or the anharmonicity $\omega''_e x''_e$ [*e.g.* [2]].

3.4. *Estimate of the R''_e and $R_e(B1)$*

The R''_e ground-state equilibrium internuclear separation was estimated using a method proposed by Liuti and Pirani [17], and Cambi *et al.* [18]. They show that properties mainly responsible for the vdW forces are the polarisabilities α of the interacting atomic partners, which therefore, also determine the long-range dispersive attraction and should be related to the molecular size. Using many examples they tested the validity of the simple relationship

$$\frac{D''_e(1)}{D''_e(2)} = \frac{C''_6(1)}{C''_6(2)} \times \left[\frac{R''_e(2)}{R''_e(1)}\right]^6 , \tag{3}$$

where the $D''_e(1)$ and $D''_e(2)$ are well-depths of molecule "1" and "2", $\mathrm{C}''_6(1)$ and $\mathrm{C}''_6(2)$ stand for their vdW constants, and $R''_e(1)$ and $R''_e(2)$ represent bond lengths of the molecule "1" and "2", respectively. To estimate the R''_e of CdXe complex we used three "reference" molecules with well known and established characteristics. Table II shows data used in the estimate. The C''_6 parameters were calculated using Slater–Kirkwood (S–K) formula [19] and corrected version of this formula proposed in Ref. [18]. According to the S–K formula $C''_6(a,b) = 3/2 \times \alpha_a\alpha_b/\left(\sqrt{\alpha_a/\mathrm{N}_a} + \sqrt{\alpha_b/\mathrm{N}_b}\right)$, where α_a and α_b are polarisabilities, and N_a and N_b are numbers of electrons in the outer shells of atoms "a" and "b", respectively. The corrections proposed in Ref. [18] introduces so called "effective electron numbers", N_{eff},

TABLE II

Estimation of the R''_e(CdXe) using method of Refs. [17] and [18]

.

Reference molecule	$D''_e[\mathrm{cm}^{-1}]$	R''_e [Å]	C''_6 [au]$^{(a)}$	C''_6 [au]$^{(a)}$ corrected	R''_e (1) [Å]$^{(a)}$	R''_e (2) [Å]$^{(a)}$
HgNe	41.4$^{(b)}$	3.89$^{(b)}$	28.85	37.8	4.20	4.21
HgAr	133.7$^{(b)}$	3.99$^{(b)}$	106.43	142.6	4.20	4.22
CdAr	107.0$^{(c)}$	4.31$^{(c)}$	134.06	172.7	4.206	4.22
	R''_e(average)				4.20±0.01	4.22±0.01
CdXe	276.0	—	298.0	399.0	$R''_e(\mathrm{average}) = 4.21 \pm 0.05$	

(a) This work

(b) Ref. [29]

(c) Refs. [1,2]

defined as $(N_{\rm eff}/N_{\rm ext}) = 1 + (1 - N_{\rm ext}/N_{\rm int}) \times (N_{\rm int}/N_{\rm tot})^2$, where $N_{\rm int}$ and $N_{\rm ext}$ are numbers of total inner and outer electrons in particular atom, and $N_{\rm tot} = N_{\rm int} + N_{\rm ext}$. The $N_{\rm eff}$ describes a deviation of the effective number of electrons with respect to the overall outer electrons. Therefore, the $N_{\rm eff}$ must be calculated for the particular atom and then it should replace the value of N_a or N_b in the S–K formula. Results of our calculation are summarised in Table II. We took the average value based on all "reference" molecules and two values of the C_6'' parameters (*i.e.*, with and without corrections for the N_a and N_b values). As an average result for the ground-state equilibrium internuclear separation we obtained $R_e'' = (4.21 \pm 0.05)$ Å. It can be seen from Table II that the correction introduced into the S–K formula makes the C_6'' coefficients larger by approximately 30% on average but this change is not reflected in the final values for the R_e'', which differ by a mere 0.2%. In Section 3.1 we reported the difference $\Delta R_e = R_e'(B1) - R_e'' = (0.05 \pm 0.01)$ Å as the result of simulation of the $B1 \leftarrow X0^+$ excitation spectrum. Using the ΔR_e, we can estimate the absolute value for the equilibrium internuclear separation of CdXe molecule in its $B1$ state as $\mathrm{R}_e'(B1) = (4.26 \pm 0.05)$ Å. The spectroscopic parameters, which contribute to the overall characterisation of the $X0^+$ and $B1$ states are shown in Table IV. Our result is very different from that reported by Helmi *et al.* [3]. For the $B1$ and $X0^+$ states they reported $D_e' = (152 \pm 15)\,\mathrm{cm}^{-1}$ and $D_e'' = (192 \pm 18)\,\mathrm{cm}^{-1}$, respectively. In order to confirm that those results cannot be correct we did the following. We accurately measured the $\nu_{00}(B1)$ energy and from Ref. [1] we deduced the $\nu_{00}(A0^+)$ for the $A0^+$ state (this value is consistent with our earlier estimate shown in Table IV). Both quantities can be combined with the result of Ref. [3] in the simple relationship

$$\nu_{00}(A0^+) + D_0'(A0^+) = \nu_{00}(B1) + D_0'(B1)\,. \tag{4}$$

Substituting the values of ν_{00} and $D_e'(B1) = 152\,\mathrm{cm}^{-1}$, for the $D_0'(A0^+)$ dissociation energy we obtained a value of $1105\,\mathrm{cm}^{-1}$, *cf.* $988\,\mathrm{cm}^{-1}$ from Ref. [3]. Similarly, when $D_e'(A0^+) = 988\,\mathrm{cm}^{-1}$ is used and the small correction of $\omega_e'/2$ is introduced ($D_0' = D_e' - \omega_e'/2$), then $D_0'(A0^+) = 962\,\mathrm{cm}^{-1}$, and finally, we arrive at $D_0'(B1) = 9.3\,\mathrm{cm}^{-1}$ which cannot be correct. It is possible to perform a similar test with respect to the value of the ground-state bond strength. The appropriate sums are

$$E_{\rm at}(^3P_1) + D_0'' = \nu_{00}(B1) + D_0'(B1)\,, \tag{5a}$$

$$E_{\rm at}(^3P_1) + D_0'' = \nu_{00}(A0^+) + D_0'(A0^+)\,. \tag{5b}$$

Using results of Ref. [3] (with the appropriate small corrections for $\omega_e'/2$ in the $B1$ and $A0^+$ states) and substituting into (5a) and (5b), we obtained $D_0'' = 184\,\mathrm{cm}^{-1}$ by substituting $D_0'(B1) = 143\,\mathrm{cm}^{-1}$, and $D_0'' = 50.1\,\mathrm{cm}^{-1}$ by substituting $D_0'(A0^+) = 962\,\mathrm{cm}^{-1}$. Again, we obtained two different values for the same molecular characteristic. The results of the present study are also in conflict with those of Breckenridge and his group (*i.e.*, Kvaran *et al.* [1], and Funk and Breckenridge [2]). Moreover, they do not corroborate the result of Helmi *et al.* [3]. Therefore, we decided to examine the $A0^+ \leftarrow X0^+$ transition, repeating the experiment carried out in Ref. [1].

3.5. Excitation spectrum of the A0$^+$ ← X0$^+$ transition

Excitation spectrum of the $A0^+ \leftarrow X0^+$ transition was observed under different conditions to those of the $B1^+ \leftarrow X0^+$ transition. We used a mixture of Xe in pure Ne [He] but with a smaller fraction of Xe. Therefore, a much higher total pressure of the carrier gas was used and, as a result several components of CdNe [6] [CdHe [4]] $A0^+ \leftarrow X0^+$ transition were seen in the recorded excitation spectrum. The spectrum is presented in Fig. 4(a). All recorded v'-bands are listed in Table III. We accepted the v'-assignment of Ref. [1]. As can be seen in Fig. 4(a) the isotope splitting inside the v'-bands was partially resolved and well reproduced (*e.g.* for $v' = 19$, see Fig. 5) by taking account of the various isotopomers of CdXe. The B–S analysis of the spectrum is shown in Fig. 3(a). It yielded values of ω_e', $\omega_e'x_e'$, D_e' and v_D'. Simulation and graphical methods also provided the $\nu_{00}(A0^+)$ energy.

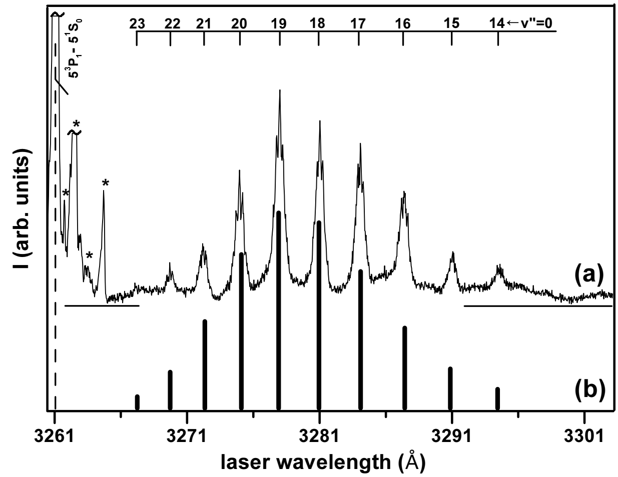

Fig. 4. Excitation spectrum of the $A0^+ \leftarrow X0^+$ transition in CdXe. 1% Xe in pure Ne mixture used as a carrier gas. (a) Experimental trace, (b) theoretical simulation of the spectrum (F–C factors). Morse functions were assumed to represent the excited and ground states;CdNe bands depicted with asterisks. A similar spectrum (although with slightly weaker $v' \leftarrow v'' = 0$ components and without the CdNe bands) was obtained with 5% Xe in pure He mixture used as a carrier gas.

TABLE III

Vibrational components of the $v' \leftarrow v''=0$ progression of the $A0^+ \leftarrow X0^+$ transition in CdXe molecule.
[λ and ν are stated in air and vacuum, respectively.]

$v' \leftarrow v''=0$	λ [Å]	ν [cm^{-1}]
14	3294.6	30343.5
15	3290.9	30376.9
16	3287.6	30407.9
17	3284.2	30439.9
18	3282.0	30469.5
19	3277.9	30497.9
20	3275.0	30525.0
21	3272.2	30550.8
22	3269.6	30575.4
23	3267.1	30598.7
24	3264.8	30620.7

"Hot" bands*

$v' \leftarrow v''=1$	λ [Å]	ν [cm^{-1}]	$\Delta\nu$ [cm^{-1}]
15	3294.3	30345.8	$\Delta\nu\,\{\nu_1(15 \leftarrow 0) - \nu_2(15 \leftarrow 1)\} = 31.1$
16	3291.1	30376.0	$\Delta\nu\,\{\nu_1(16 \leftarrow 0) - \nu_2(16 \leftarrow 1)\} = 31.0$

"Hot" bands assigned with an aid of the simulation procedure assuming Morse representations for the $A0^+$ and $X0^+$ energy states.

A thorough simulation procedure based on the calculation of F–C factors yielded a value for $\Delta R_e = R'_e(A0^+) - R''_e$ and confirmed our earlier assumption on the value of $\nu_{00}(A0^+)$. The calculated F–C factors are shown in Fig. 4(b). The result of the B–S analysis is summarized in Table IV and compared with that of Kvaran *et al.* [1]. It shows that our new values for spectroscopic constants are close to those measured earlier, however when we employ Eq. (5b) and substitute values of Table IV we obtain $D''_0 = 189.1$ cm^{-1}, which is too small when compared with the results discussed above. Evidently, there is a region in the spectrum at the large v' side (*i.e.*, for $R \gg R'_e$, near the dissociation limit), which does not obey the linear B–S approximation.

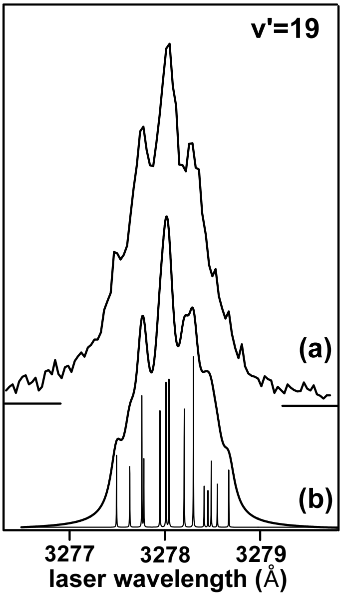

Fig. 5. (a) Partially resolved isotopic structure of the $A0^+(v'=19) \leftarrow X0^+$ band, and (b) gross structure of the $v'=19$ band and its isotopic structure simulated using a Lorentzian laser convolution function with spectral width corresponding to $1.4\,\mathrm{cm}^{-1}$ and $0.15\,\mathrm{cm}^{-1}$ (FWHM), respectively.

As stated above, the B–S method tends to decrease the true values of the dissociation energy. In our case the difference is about 6% with respect to the result that we believe to be correct. In order to justify our reasoning, we applied the limiting LR–B method [15,16] to the raw data of this study and this yielded the graphical result presented in Fig. 3(b). As shown, the energy D' at the dissociation limit is the same as that obtained from the analysis of the $B1 \leftarrow X0^+$ transition. We consider this a plausible result since both $A0^+$ and $B1$ excited states are asymptotically correlated to the same 5^3P_1 Cd-atomic asymptote. For a more exact analysis, close to the dissociation of the $A0^+$-state, we employed a generalized Near Dissociation Expansion (NDE) method and used a G_vNDE program of LeRoy [20]. A detailed description of this method will not be repeated here. However, it is necessary to state that the program for fitting vibrational energies to the NDE allows to determine the long-range potential characteristics, even when the close-to-dissociation limit vibrational transitions are not measured in the experiment. The G_vNDE program proved itself to be a useful tool supplementing the B–S and the limiting LR–B methods [6,7,9,21]. As input parameters we used the measured $E_{v'}$ energies of the $A0^+$ state, the value for the dissociation limit D' (as from the analysis of the $B1 \leftarrow X0^+$

TABLE IV

Spectroscopic constants of the $X0^+$, $B1$ and $A0^+$ states of CdXe molecule. All constants are stated in [cm^{-1}] unless specified otherwise.

Designation	$X0^+(5^1S_0)^{(\mathrm{a})}$	$B1(5^3P_1)^{(\mathrm{b})}$	$A0^+(5^3P_1)^{(\mathrm{c})}$	$A0^+(5^3P_1)^{(\mathrm{a})}$
ω_0	32.1 ± 0.3	18.0 ± 0.2	—	51.4 ± 0.4
$\omega_0 x_0$	0.99 ± 0.01	0.37 ± 0.01	—	0.6 ± 0.01
D_0	259.7 ± 5.0 $176 \pm 5^{(\mathrm{d})}$ $259.0^{(\mathrm{c})}$	218.9 ± 5.0	1170.8 ± 10.0 $1171.6^{(\mathrm{e})}$ $1171 \pm 7.3^{(\mathrm{f})}$	1101 ± 10
ω_e	33.1 ± 0.6	18.3 ± 0.3	—	52.3 ± 0.5; $50.7^{(\mathrm{g})}$
$\omega_e x_e$	0.99 ± 0.01	0.37	—	0.60 ± 0.01; $0.6^{(\mathrm{g})}$
D_e	276 ± 5 $192 \pm 18^{(\mathrm{h})}$	227.9 ± 5.0 $152 \pm 15^{(\mathrm{h})}$	1196 ± 10 $1197.5 \pm 8.9^{(\mathrm{f})}$	1127 ± 11 $1086 \pm 40^{(\mathrm{g})}$ $988 \pm 41^{(\mathrm{h})}$
ΔR [Å]	—	$+0.05 \pm 0.01$	—	-1.19 ± 0.01
R_e [Å]	$4.28^{(\mathrm{h})}$ $4.21 \pm 0.05^{(\mathrm{i})}$	$4.41^{(\mathrm{h})}$ $4.26 \pm 0.05^{(\mathrm{i})}$	—	$3.02 \pm 0.05^{(\mathrm{i})}$
ν_{00}	—	$30696.8 \pm 1.0^{(\mathrm{a})}$	—	29744.1 ± 1.0
T_{vib} [K]	70	70	—	30
D'	—	30915 ± 5	30915 ± 5	—
v_D	16	24	$59^{(\mathrm{f})}$	42
C_6'' $\times 10^6$ [cm^{-1} Å^6]	$1.437^{(\mathrm{j})}$; $1.922^{(\mathrm{k})}$	—	—	—

(a) From the "best fit" of simulated spectra and from B–S analysis;

(b) From "hot" bands of the $B1 \leftarrow X0^+$ transition with assumption of a Morse potential;

(c) From LR–B analysis, Refs. [15, 16];

(d) Ref. [2];

(e) Eq. (5);

(f) From G_vNDE program, Ref. [20];

(g) Ref. [1];

(h) Ref. [3];

(i) Calculated using correlation method and ΔR_e from the "best fit" of the F–C factors;

(j) Calculated using S–K formula, Ref. [19];

(k) As in (j) but obtained with an aid of corrections proposed by Cambi *et al.* [18]. Polarizablities α_{Cd}=49.7 au and α_{Xe}=27.3 au were taken from Ref. [30] and Ref. [31], respectively.

transition), and an estimate for the $C_6'(A0^+)$ vdW constant. We evaluated the latter in a semi-empirical way from the work of Grycuk and coworkers cited in Ref. [22], which reports experimental results for ΔC_6. According to these authors $\Delta C_6 = C_6'(B1) - C_6'' = 150\,\mathrm{au}$. We took our ground-state C_6'' coefficient from Table II and, therefore, as an input value we tested the $C_6'(A0^+)$ in the range from 540 au to 620 au. We obtained the best result for $C_6'(A0^+) \approx 580\,\mathrm{au}$ (*i.e.*, $2.9 \times 10^6\,\mathrm{cm}^{-1}\,\text{Å}^6$). The results of G_vNDE analysis are listed in Table IV. They are consistent with the result of the limited LR–B analysis. The dissociation energies are about 6% larger than those obtained using the B–S method. It is easy to see that all the values are in good agreement and they yield the same value for the ground-state dissociation energy.

4. Conclusions

Two independent experiments have been performed to characterise for the first time the $B1$ excited and $X0^+$ ground states as well as to correct characterisation of the $A0^+$ excited state of CdXe molecule. Table IV collects all results obtained from the analysis of the CdXe excitation spectra related to both molecular states correlating to the 5^3P_1 Cd-atomic asymptote. For comparison, it lists also results reported in Refs. [1–3]. The successful characterisation of the CdXe ground state completes the description of the CdRG family. Taking into consideration the ground-state dissociation energies of *all* molecules within this family, we may arrive at interesting conclusions as it was shown in Ref. [8]. If we plot the D_e'' values for various CdRG complexes *versus* polarizabilities of the RG atomic partners we obtain a linear dependence with a well defined slope $D_e''/\alpha_{\mathrm{RG}}$ as it is shown in Fig. 6.

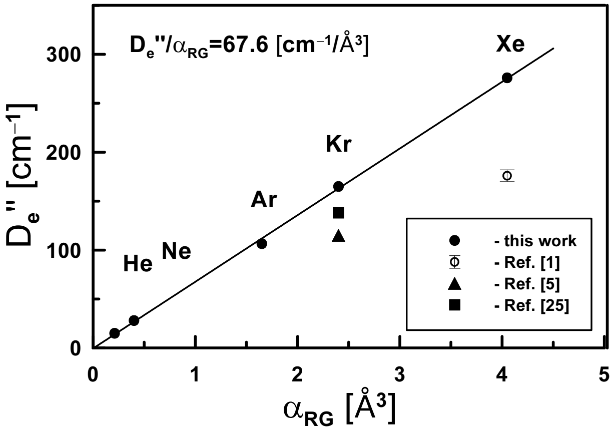

Fig. 6. Dissociation energy, D_e'', plotted *versus* RG polarizability, α_{RG}.

Such a dependence has been observed previously [8,21] and it may be explained partially on the basis of a simple theoretical description of the dispersion interaction within a London–Drude model of vdW complexes [8,23]. We believe this empirical result expresses a general property of molecules within which neutral atom–neutral atom interaction is in effect only, and it may be a useful tool for estimation of an unknown bond strengths within other families of vdW complexes of such a kind. We consider this behaviour to be also true with respect to the ZnRG [21,23] and HgRG [23,25,27] families of vdW molecules. To support this statement, we refer to Fig. 6. It can be seen that the CdKr dissociation energy, as reported in Refs. [1,5], shows a considerable departure from the linear dependence. We examined this discrepancy very carefully, repeating previous investigations using better experimental tools, and we were able to show [9] that the ground-state dissociation energy of the CdKr molecule was most probably erroneously evaluated in the past. Our corrected value of D_e''(CdKr) is consistent with the value of 67.6 $\mathrm{cm}^{-1}\mathrm{\AA}^{-3}$ defined by the slope of the graph in Fig. 6. A theory of dispersion-forces [26] lead us to a conclusion [8] (which appears to be correct for the case of the CdRG and ZnRG molecules) that the R_e'' equilibrium internuclear distance of the vdW complexes is decreasing slowly as the RG atom becomes heavier. However, this observation seems to fail in the case of the HgRG molecules [23]. This may suggest that some more complicated mechanisms of interaction are to be involved. Indeed there is a possibility of some ionic interaction of the outer electronic shells and the positively charged atomic cores [23,27,28].

This research was supported by the Polish State Committee for Scientific Research (KBN) grant no. 2 P03B 037 20 (J.K. and M.Ł., experiment in Kraków) and by the Natural Science and Engineering Research Council of Canada (J.K. and M.C., experiment in Windsor).

REFERENCES

[1] A. Kvaran, D.J. Funk, A. Kowalski, W.H. Breckenridge, *J. Chem. Phys.* **89**, 6069 (1988).

[2] D.J. Funk, W.H. Breckenridge, *J. Chem. Phys.* **90**, 2927 (1989).

[3] M.S. Helmi, T. Grycuk, G.D. Roston, *Chem. Phys.* **209**, 53 (1996).

[4] J. Koperski, M. Czajkowski, *J. Chem. Phys.* **109**, 459 (1998); J. Koperski, M. Czajkowski, *Chem. Phys. Lett.* **350**, 367 (2001).

[5] A. Kowalski, M. Czajkowski, W.H. Breckenridge, *Chem. Phys. Lett.* **121**, 217 (1985); R. Bobkowski, M. Czajkowski, L. Krause, *Phys. Rev.* **A41**, 243 (1990); M. Czajkowski, R. Bobkowski, L. Krause, *Phys. Rev.* **44**, 5730 (1991); *Phys. Rev.* **45**, 6451 (1992).

[6] J. Koperski, M. Czajkowski, *Eur. Phys. J.* **D10**, 363 (2000).

[7] J. Koperski, S.M. Kiełbasa, M. Czajkowski, *Spectrochim. Acta Part A* **56**, 1613 (2000).

[8] M. Czajkowski, L. Krause, R. Bobkowski, *Phys. Rev.* **A49**, 775 (1994).

[9] J. Koperski, M. Łukomski, M. Czajkowski, in: *Spectral Line Shapes*, Vol. 11, 15th ICSLS, Ed. J. Seidel, AIP Conference Proceedings Vol. 559, American Institute of Physics, Melville, New York 2001, p. 304–306; J. Koperski, M. Łukomski, M. Czajkowski, *Spectrochim. Acta Part A* (2002) in press.

[10] L.B. Lubman, C.T. Rettner, R.N. Zare, *J. Phys. Chem.* **86**, 1128 (1982).

[11] M. Czajkowski, R. Bobkowski, L. Krause, *Phys. Rev.* **A40**, 4338 (1989); M. Czajkowski, J. Koperski, *Spectrochim. Acta Part A* **55**, 2221 (1999).

[12] R.D. van Zee, S.C. Blankenspoor, T.S. Zwier, *J. Chem. Phys.* **88**, 4650 (1988).

[13] J. Koperski, J.B. Atkinson, L. Krause, *Chem. Phys. Lett.* **219**, 161 (1994).

[14] *Atomic Energy Levels*, Ed. C.E. Moore, Natl. Bur. Stand. U.S. NSRDS No. 35, U.S. GPO, Washington, DC, 1971.

[15] R.J. LeRoy, R.B. Bernstein, *J. Chem. Phys.* **52**, 3869 (1970).

[16] R.J. LeRoy, R.B. Bernstein, *J. Molec. Spectrosc.* **37**, 109 (1971).

[17] G. Liuti, F. Pirani, *Chem. Phys. Lett.* **122**, 245 (1985).

[18] R. Cambi, D. Cappalletti, G. Liuti, F. Pirani, *J. Chem. Phys.* **95**, 1652 (1991).

[19] J.C. Slater, J.G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

[20] R.J. LeRoy, *J. Chem. Phys.* **101**, 10217 (1994).

[21] J. Koperski, M. Czajkowski, *Phys. Rev.* **A62**, 012505 (2000).

[22] S.H. Brym, *Habilitation Thesis*, Pedagogical University, Olsztyn 1996, p. 101, Table 6.3 (in Polish).

[23] J. Koperski. *Phys. Rep.* (2002), in press.

[24] K. Yamanouchi, J. Fukuyama, H. Horiguchi, S. Tsuchiya, K. Fuke, T. Saito, K. Kaya, *J. Chem. Phys.* **85**, 1806 (1986).

[25] J. Koperski, J.B. Atkinson, L. Krause, *J. Mol. Spectrosc.* **207**, 172 (2001).

[26] G.C. Maitland, M. Rigby, E.B. Smith, W.A. Wakeham, *Intermolecular Forces*, Clarendon Press, 1987.

[27] D.J. Funk, A. Kvaran, W.H. Breckenridge, *J. Chem. Phys.* **90**, 2915 (1989).

[28] C. Jouvet, C. Lardeux-Dedonder, S. Martrenchard, D. Solgadi, *J. Chem. Phys.* **94**, 759 (1991).

[29] J. Koperski, J.B. Atkinson, L. Krause, *Chem. Phys.* **186**, 401 (1994).

[30] D. Goebel, U. Hohm, *Phys. Rev.* **A52**, 3691 (1995).

[31] *Handbook of Chemistry and Physics*, Ed. D.R. Lide , 72nd edn, RCR Press, 1991-1992; *Science Data Book*, Ed. R.M. Tennent, Oliver & Boyd, Edinburgh 1976; T.M. Miller, B. Bederson, *Adv. At. Mol. Phys.* **13**, 1 (1977).