Spectroscopical study of CdKr and Cd$_2$ molecules in extreme conditions: vibrationally and rotationally cold vdW molecules.

M. Łukomski$^1$, J. Koperski $^2$
Instytut Fizyki, Uniwersytet Jagielloński, ul. Reymonta 4, 30-059 Kraków, Poland
$^1$ lukomski@theta.uoks.uj.edu.pl, $^2$ ufkopers@cyf-kr.edu.pl

M. Czajkowski$^3$
Department of Physics, University of Windsor, Windsor, Ont., N9B 3P4, Canada
$^3$ mczajko@uwindsor.ca
Supersonic expansion beam is a source of vibrationally and rotationally cold molecules that can be investigated using methods of laser spectroscopy.

Molecules in a supersonic beam are irradiated with a second harmonic output from a Nd:YAG laser-pumped dye laser. The resulting total fluorescence emitted perpendicularly to both molecular and laser beams is recorded with photomultiplier coupled with BOXCAR system or digital scope and stored in a computer.

Measured signal was a source of information about properties of van der Waals (vdW) molecules in such extreme conditions. A rigorous analysis of excitation and fluorescence spectra, based on Birge–Sponer and Le Roy–Bernstein methods allow to find analytical functions which describe potential energy curves of investigated molecular states. Further investigation allows to determine long-range potential curve parameters, and in the case when the molecular states can not be approximated by Morse representation an Inverse Perturbation Approach method was used to resolve the radial Shrödinger equation and, in consequence, to find a real shape of the potential curve. To complete information about properties of the molecules and about supersonic expansion environment, measurement of fluorescence-decay signals as a function of time was made, using method of single-photon counting. It provided us information about lifetime of excited states in different regions of molecular beam.

All results obtained in this work are compared with those of other experiments and theoretical studies.

A financial assistance of the KBN (grant 5 P03B 037 20), Institute of Physics, Jagiellonian University (grant 2000) is acknowledged.
THE SUPERSONIC EXPANSION BEAM

P₀, T₀

M << 1

d

Mₜ

Meff

Xₜ

Xeff

X_M

source

BARREL SHOCK

MACH DISK SHOCK

zone of silence

M >> 1

M < 1

JET BOUNDARY
**supersonic beam** → source of ro–vibrationally **cold** vdW molecules

at room and higher temperatures

population of ro-vibrational levels given by Boltzman distribution

in a supersonic beam

all population of ro-vibrational levels in lowest (v,J) state

**vdW molecules** → atoms bound by very week vdW forces

- $D_0$ very small (~ 10–100 cm$^{-1}$)
- may exist in supersonic beam
- $T_{rot}$, $T_{osc}$ very low (~ 10–100 K)

**Laser spectroscopy of vdW complexes in supersonic beam**

→ simplification of excitation spectra (excitation from lowest (v,J) states)

→ very week vdW interactions can be investigated

→ determination of potential energy $U(R)$ curves
Birge–Sponer plot

*Phys. Rev.* **28**, 259 (1926)

Plot $\Delta G_{v+1/2}$ against $(v+1/2)$

- gives: $\omega_0$ and $\omega_0 x_0$

**LeRoy-Bernstein method**


Assumption: $V(R) = D - C_n/R^n$ in long-range limit (given $n$)

Plot $(\Delta G_v)_{\text{aver}}^{2n/(n+2)}$ against $E(v)$

- gives: $D$

Plot $(D - E(v))^{(n-2)/2n}$ against $v$

- gives: $v_D$ and $C_n$

**Near-Dissociation-Expansion program**


- gives: realistic estimates for $D$, $v_D$ and $C_n$
CdKr: $D_1(v'=16) \times X_0^+$

LIF (arb. units)

monochromator wavelength ($\Delta$)

experimental

simulation
M-S: $n_0=8.68$, $n_1=9.91$

FLUORESCENCE SPECTRUM

CdKr: $D_1(v'=16) \times X_0^+$

(a) 3.2 $\Delta$/mm (0.4mm slit-width)
(b) 1.6 $\Delta$/mm (0.2mm slit-width)
(c) 0.4 $\Delta$/mm (0.05mm slit-width)
(d) b-b and b-f simulation

LIF (arb. units)

(a) (b) (c) (d)
RESULT – X0⁺-STATE INTERATOMIC POTENTIAL

CdKr: X0⁺-bound well

CdKr: X0⁺-repulsive

CdKr: X0⁺-long range
Vibrational analysis of experimental excitation and fluorescence spectra in CdKr molecule was carried out. A rigorous analysis of the excitation spectra based on Birge-Sponer and LeRoy-Bernstein method lead to the X0\(^+\) - and improved A0\(^+\), B1 and D1 - state characterisation. An analysis of bound-bound and bound-free parts of the fluorescence spectrum confirmed a \(v'\) – assignment and indicated that Morse and Maitland-Smith functions are adequate representation of bound well and repulsive wall of the X0\(^+\) -state potential curve, respectively. We obtained characterisation of CdKr molecular states which are in excellent agreement with theoretical study of this complex.

Results of this investigations will be published soon.
NUMERICAL CONSTRUCTION OF AN ACCURATE POTENTIAL CURVE

**ab initio** CALCULATION

EXPERIMENTAL DATA

MODELLING OF THE "BEST" POTENTIAL CURVE

BIRGE-SPONER ANALYSIS

approximate potential

zeroth-order eigenvalues

NUMERICAL SOLUTION OF THE RADIAL SHRÖDINGER EQUATION

an inverse perturbation approach method applied for quantum mechanical calculation

*Mol.Spectrosc.* 56 (1975) 93
*Mol.Spectrosc.* 65 (1977) 46

THE REAL POTENTIAL ENERGY CURVE
PRELIMINARY ANALYSIS OF EXPERIMENTAL TRACE

Czuchaj & Stoll
Chem. Phys. 248 (1999) 1

5^3P

fitted Morse
fitted polynomial

experimental Morse

Experimental trace

(a) 0 ← v' = 0
(b) 4, 3, 2 ← v' = 0

R [Å]
E [cm⁻¹]

I (arb. u. units)

λLAS [Å]
MODELING OF APPROXIMATE POTENTIAL CURVE

![Graph showing potential energy as a function of R [Å]. The graph includes labeled curves (a), (b), (c), and (d). The experimental trace is indicated with vertical lines at various R values.](image)

- **(a)**
- **(b)**
- **(c)**

**Experimental Trace**: I (arb.units)

- **(d)**
THE REAL POTENTIAL ENERGY CURVE

\[ E (\text{cm}^{-1}) \]

\[ R \, [\text{Å}] \]

\[ R_{\text{in}} \quad R_{\text{b}} \quad R_{\text{out}} \]

\[ E_{\text{in}} \quad E_{\text{out}} \quad E_{\text{b}} \]

\[ 2,3 \quad 1 \quad 0=v' \]

\[ 5^3P_1 \]
THE FINAL RESULT OF NUMERICAL ANALYSIS

\[ \nu_{0,0}(\text{Cd}_2) = 30724.5 \text{ cm}^{-1} \]

\[ \nu_{0,0}(\text{CdKr}) = 30706.1 \text{ cm}^{-1} \]

\( B_1 \)

\( |0_u^+\) \n
\( X_0^+ \)

\( |X_0^+\) \n
\( R (\text{Å}) \)

\( E = 0 \text{ cm}^{-1} \)

\( E = 30811 \text{ cm}^{-1} \)

\( \nu_{0,0}(\text{CdKr}) = 30706.1 \text{ cm}^{-1} \)

\( \nu_{0,0}(\text{Cd}_2) = 30724.5 \text{ cm}^{-1} \)

[Graph showing spectral lines and transitions]
An analysis of the $B1(5^3P_1) \leftarrow X0^+(5^1S_0)$ transition in CdKr vdW molecule, in view of the recent result of \textit{ab initio} calculation, allowed for modelling of the B1-state interatomic potential with relatively high precision as compared to limited experimental evidence. An inverse perturbation approach method was applied for quantum mechanical calculation. The method, with only twelve experimentally observed transition energies observed in this study, required a careful preparation of the shape of “starting” hybrid PE curve. Ultimately, the PE curve of the B1 excited state was derived. The simulation of the CdKr excitation spectrum using the determined B1-state potential, produced transition frequencies that are in excellent agreement with those observed experimentally. Differences in the distribution of F-CF intensities are attributed to the substantial contribution of the Cd$_2$ vibrational components in the investigated spectrum.

Results of this investigations will be published soon.
Example of fluorescence decay signal as a function of time (CdAr: B1 (v'=2) \rightarrow X0^+).
RESULTS FROM SINGLE PHOTON COUNTING EXPERIMENT

Cd₂ \( v' = 2 \)
Cd₂ \( v' = 1 \)
Cd₂ \( v' = 0 \)

Cd₂: \( 1_u(5^3P_2) \leftarrow X_0^+(5^1S_0) \)

CdAr: \( B1_v = 2 \leftarrow X0^+ \)

a)

b)

lifetimes [ns]

-distances from nozzle

\( X \) [mm]
The single photon counting experiment resulted in observation of the fluorescence decay of the selectively excited vibrational states in the $1_u(5^3P_2)$ and $B1(5^3P_1)$ electronic energy states in Cd$_2$ and CdAr molecules, respectively. The results show a distinct $v'$ and $X$ dependencies. A further improvement is planned to observe the decays in the collision-free region (“zone of silence”) of the supersonic beam.

Experiments planned in the future, allow us to determine lifetimes of broad class of vdW molecular states. Moreover, measurements in different regions of molecular expansion beam allow us to determine properties of supersonic molecular beam environment.
Fig 3

Fig 4
Schematic diagram of a cross-section of the supersonic expansion beam. M – Mach numbers: $M_{\text{eff}}$ – effective, $M_T$ – terminal; $X_{\text{eff}}$, $X_T$ – corresponding distances from the nozzle; $X_M$ – distance to the Mach disc shock; $P_0, T_0$ – pressure and temperature in the source; $d$ – diameter of the orifice.

Fig 13
Preliminary double-well B1-state hybrid potential of the CdKr molecule constructed according with ab initio calculated points and B-S analysis of experimental results. Below, the experimental trace of the $B1 \leftrightarrow X0^+$ transition. (a) Simulation of the $v' \leftrightarrow v''=0$ progression. Morse functions from B-S analysis were assumed to represent excited and ground states. (b) As in (a) but with assumption that Morse potential representing B1 state was fitted to ab initio calculated points in the range of the inner potential well.
Fig 18

Fig 19
1_u(5^3P_2)-state lifetime versus the v’ quantum number of the excited state; (b) B1_{v’=2} – state lifetime versus the collision number in the molecular expansion beam.

Fig 6
Potential energy (PE) curves of the X0^+(5^1S_0), B1(5^3P_1) A0^+(5^3P_1) and D1(5^1P_1) electronic energy states of CdKr molecule. The curves are drawn according to the experimentally determined parameters using Morse representation.

Fig 8
Fluorescence spectrum of the D1_{v’=16} ← X0^+ transition of CdKr molecule detected after selective excitation of the v’=16 vibrational level.

Fig 9
PE curve of the CdKr ground state constructed according to the experimental results. Three-region characterisation in the intermediate, short-, and long-range limit of internuclear separations.
Fig 14
Construction of the double-well B1-state hybrid potential of the CdKr molecule (preliminary potential and consecutive steps of construction). Below: the experimental trace of B1←X0⁺ transition compared with simulations of these transitions with assumption that following double-well hybrid and Morse functions represent the B1 and X0⁺-state, respectively.
Fig 15
The double-well B1-state potential (empty circles approximated with spline function) found as a result of calculation based on the IPA method. Full circles represent the starting (zero-order) potential. (a) Experimentally found energies and (b) eigenvalues generated for finally obtained B1-state potential.

Fig 16
(a) and (b) Experimental excitation spectrum of the B1←X0⁺ transition in CdKr (position of identified vibrational components of the 0_u⁺← X0_g⁺ transition in Cd₂ are indicated with asterisks – see also picture on the right side). (c) The simulated Franck-Condon factors (F-CF) of the v’← v”=0 progression in the B1←X0⁺ transition using the double-well PE curve obtained from the quantum mechanical calculation.