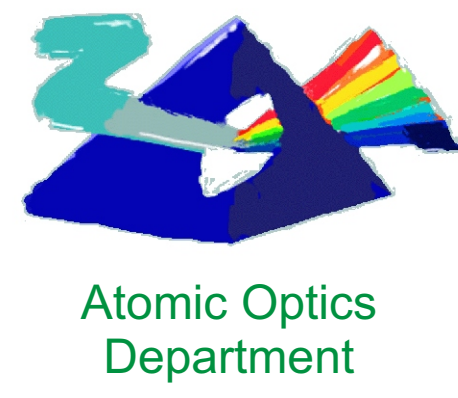


# Characterization of interatomic potentials of CdRg and Zn<sub>2</sub> molecules produced in supersonic beams

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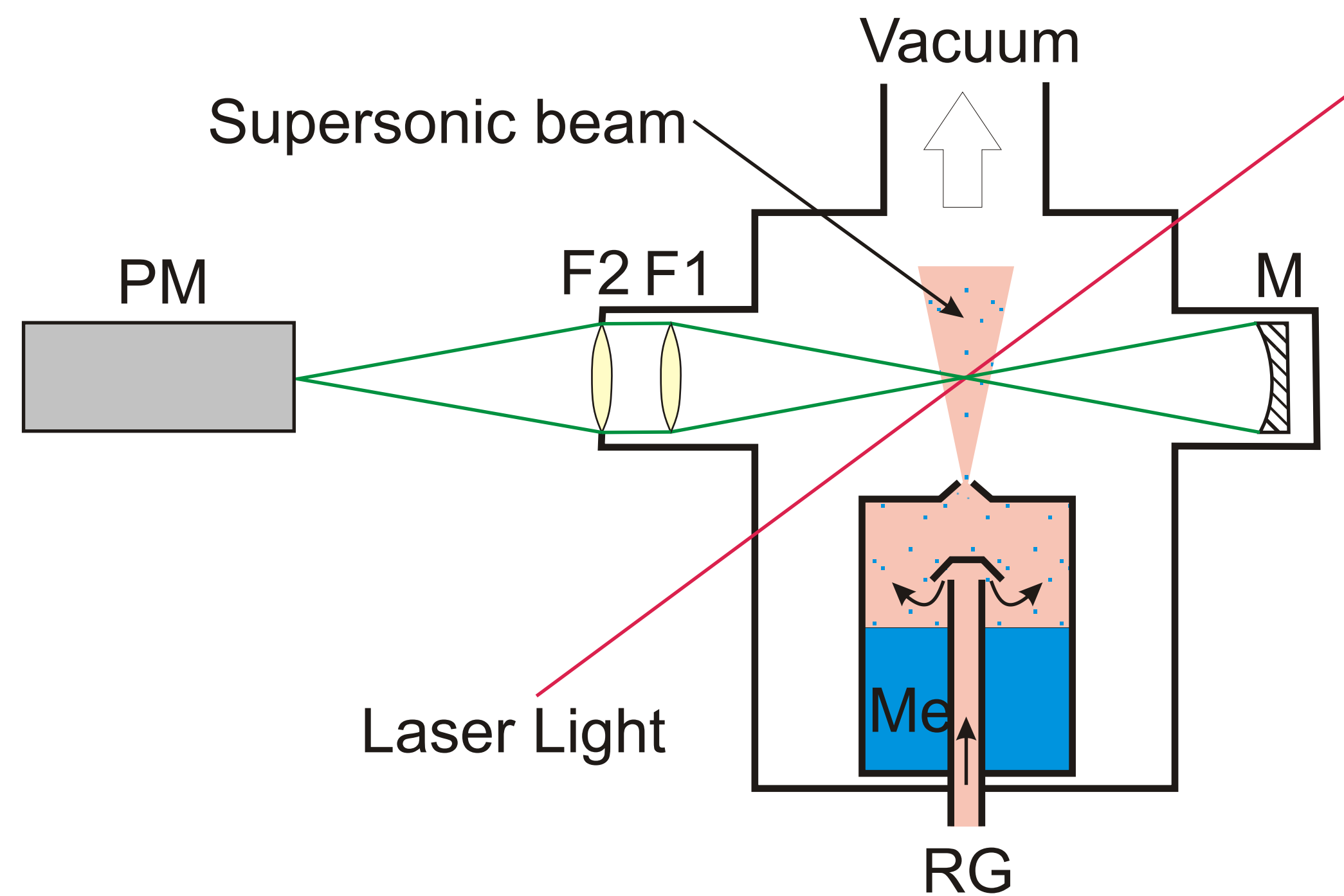


Fig. 1. Experimental setup used in the studies. RG - rare gas at high pressure (3-13 Bar); Me - melted metal (Cd or Zn); M - R=100% concave mirror; F1, F2 - lenses; PM - photomultiplier;

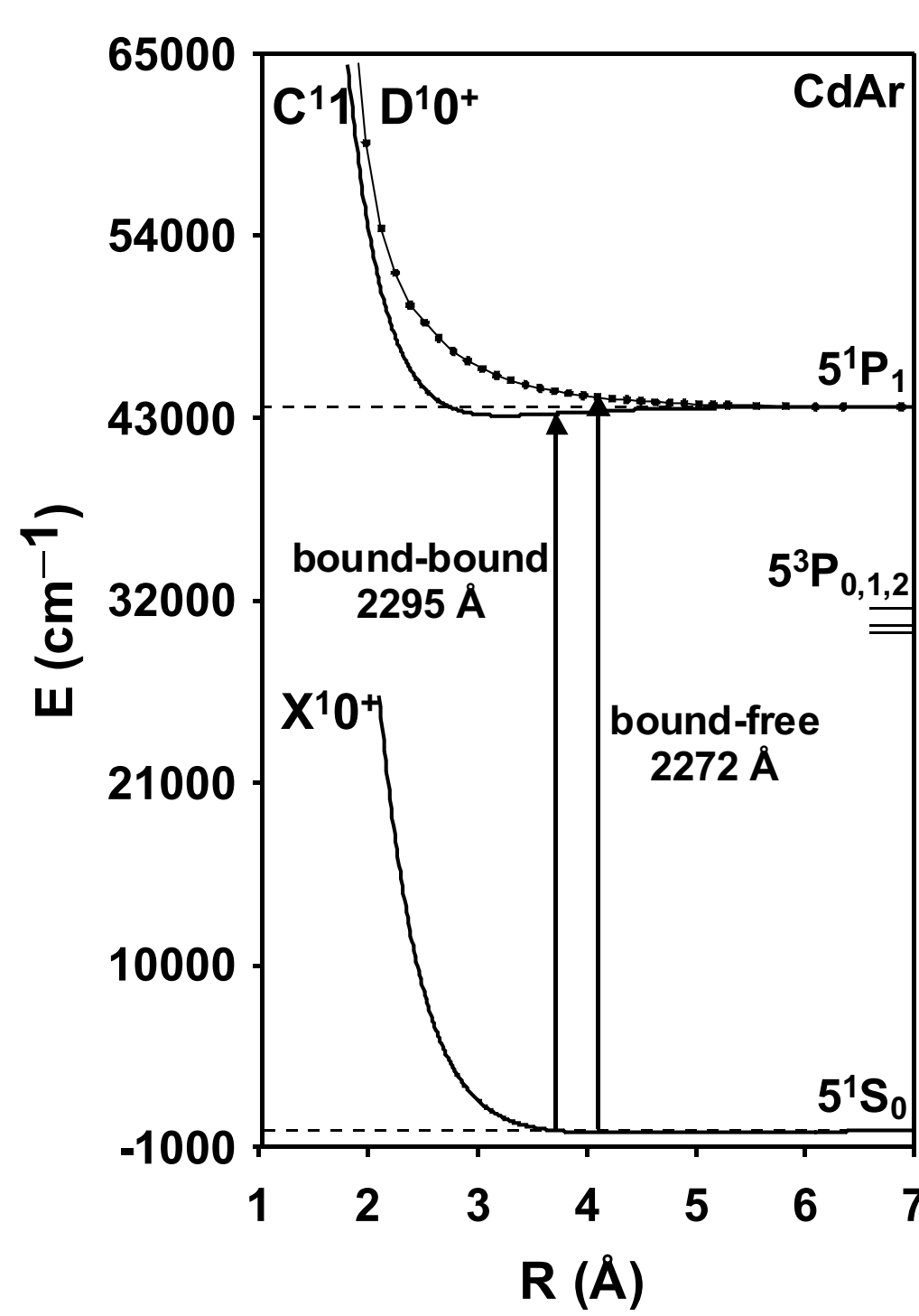
## ABSTRACT:

The supersonic beam method<sup>1-4</sup> combined with techniques of laser spectroscopy has been used for determination of the excited-state interatomic potentials of the heteronuclear CdRg (Rg=rare gas: Ar and Kr) and homonuclear Zn<sub>2</sub> van der Waals (vdW) molecules. In the experiments, the CdRg or Zn<sub>2</sub> molecules were produced in a free-jet supersonic beam. The dimers were excited with a dye-laser beam in a vacuum chamber and the resulting total fluorescence emitted perpendicularly to the direction of the molecular and laser beams was recorded with a photomultiplier. Unstructured bound-free profiles in the CdRg that were first-time detected in the excitation at D'0'(<sup>1</sup>Σ<sup>+</sup>)←X'0'(<sup>1</sup>Σ<sup>+</sup>) transition as well as well-resolved bound-bound vibrational transitions in the Zn<sub>2</sub> detected at the <sup>3</sup>0<sub>u</sub><sup>+</sup>(<sup>1</sup>Π<sub>u</sub>)←X'0<sub>g</sub><sup>+</sup>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) transition are presented. Analysis of the bound-free excitation spectra yielded information on the repulsive wall of the D'0'-state potential in CdAr and CdKr, whereas analysis of the bound-bound excitation spectra lead to the determination of the <sup>3</sup>0<sub>u</sub><sup>+</sup>-state potential parameters in Zn<sub>2</sub>.

## Experimental Setup:

In the supersonic beam (see Fig. 1) a metal (cadmium or zinc) is heated in an oven well above the melting point to produce the metal vapor under a sufficient pressure. At the same time, a carrier rare gas under considerably high pressure (3-13 bar) is applied. The gas with seeded metal atoms is passing out into a vacuum through a small orifice (diameter D~0.2 mm). Due to the collisions in the orifice, weakly bound CdRg or Zn<sub>2</sub> molecules, respectively, are formed and adiabatic cooling of internal degrees of freedom is taking place. Consequently, only the lowest ro-vibrational ground-state levels are populated allowing for a considerable simplification of the excitation spectra which are produced by crossing the laser beam at certain distance from the orifice and by scanning the laser frequency through the ro-vibrational transitions. The resulting total fluorescence is observed in the direction perpendicular to the plane containing the molecular and laser beams. The excitation geometry reduces the Doppler broadening. This reduction is limited by supersonic beam geometry as the beam is not well collimated.

Fig. 2. Investigated electronic transitions in CdAr molecule. CdAr interatomic potentials involved in the studied transition along with the C'1 potential that correlates to the same 5<sup>1</sup>P<sub>1</sub> atomic asymptote. The D'0'-state potential is represented with *ab-initio* points of Czuchaj and Stoll<sup>6</sup>. The bound-free (centered at 2272 Å) and bound-bound (centered at 2295 Å) transitions are depicted. For the CdKr molecule the diagram and transition wavelengths are similar.



## Fitting method CdRG dimers:

To fit the analytical potentials to the experimental result a BCONT program of LeRoy<sup>5</sup> has been used. The initial parameters for the program were taken from result of *ab-initio* calculation performed by Czuchaj and Stoll<sup>6</sup>. In the case of a Morse potential, the initial parameters were obtained by fitting the Morse function to those *ab-initio* points, which values were less than 800 cm<sup>-1</sup> and for which the interatomic distance was less than 8 Å. During the fit to the experimental results, the D<sub>e</sub> was kept fixed to ensure the fitting procedure to be completed successfully.

In the case of a Born-Mayer potential, the fitting method was similar. The main difference was that original Born-Mayer potential did not produce an acceptable fit to the *ab-initio* points and experimental results, therefore the potential was modified by adding a constant value:  $U(R) = A \exp(-b \cdot R) - C_0$ . Finally, using the corrected potential, the initial parameters were calculated by fitting the Born-Mayer function to the *ab-initio* points for the interatomic distance from 3.8 Å to 5.0 Å. This particular distance was selected because the wave function of the initial state X'0' (<sup>1</sup>Σ<sup>+</sup>) v'=0 in the excitation, allow to "probe" only this part of the excited-state potential. The options available in the BCONT program did not allow to modify the C<sub>0</sub> parameter during the fitting procedure.

As can be seen in Figs. 4,6 both Morse and Born-Mayer curves in CdAr and CdKr molecules within interesting interatomic range of 3.8-5 Å are almost identical. Therefore in Figs. 3,5 we used that simulated spectrum reconstructs well experimental result. This indicates that used method is accurate.

## Zn<sub>2</sub> dimer:

For the <sup>3</sup>0<sub>u</sub><sup>+</sup> (<sup>1</sup>Π<sub>u</sub>) state in Zn<sub>2</sub>, the interatomic potential has been determined using a Birge-Sponer interpolation method and calculation of the Franck-Condon factors to satisfactory reconstruct the registered spectrum.

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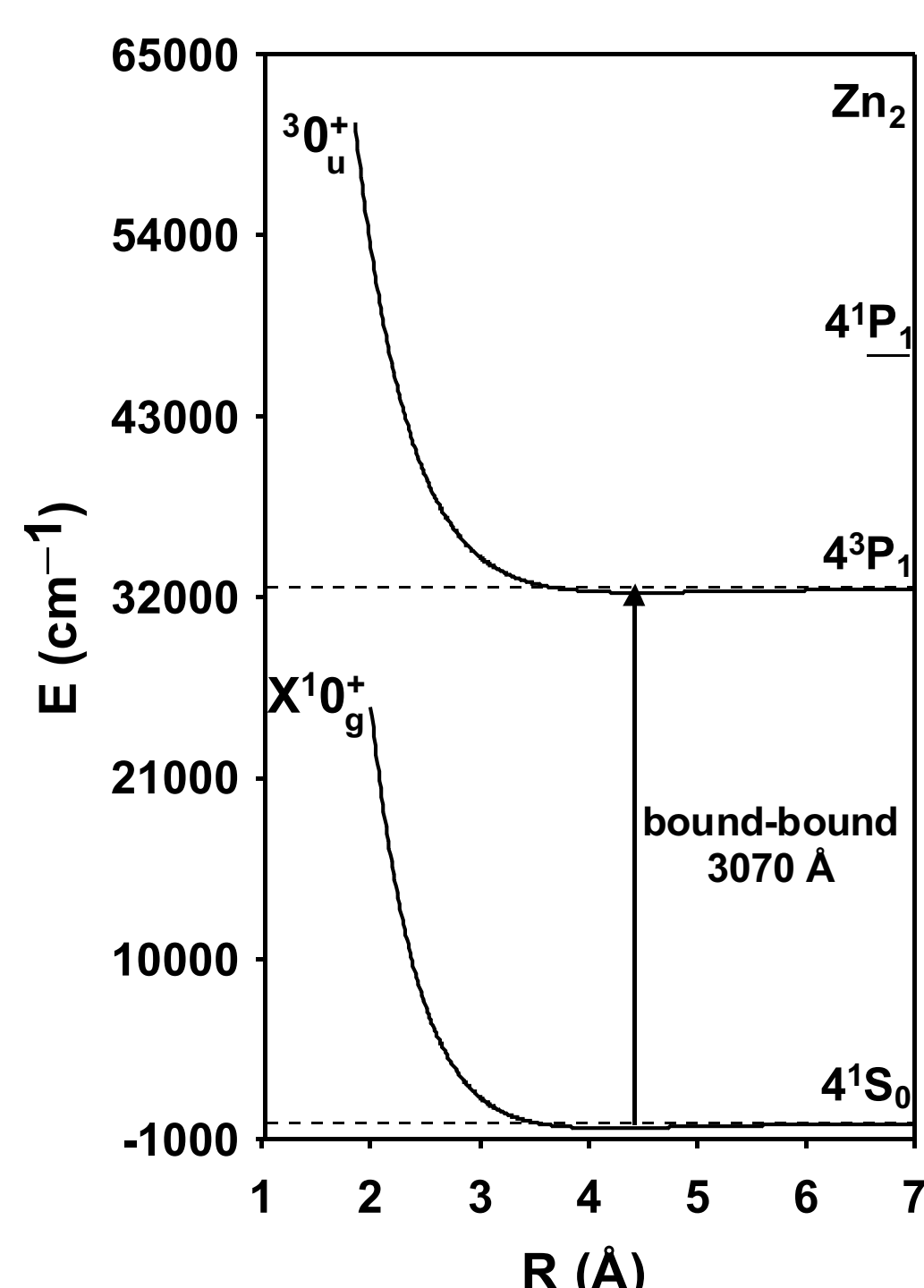


Fig. 7. The Zn<sub>2</sub> interatomic potentials involved in the studied transition. The bound-bound (centered at 3070 Å) transitions are depicted. Interatomic potentials for the Zn<sub>2</sub> have been *ab-initio* calculated by Czuchaj *et al.*<sup>11</sup>.

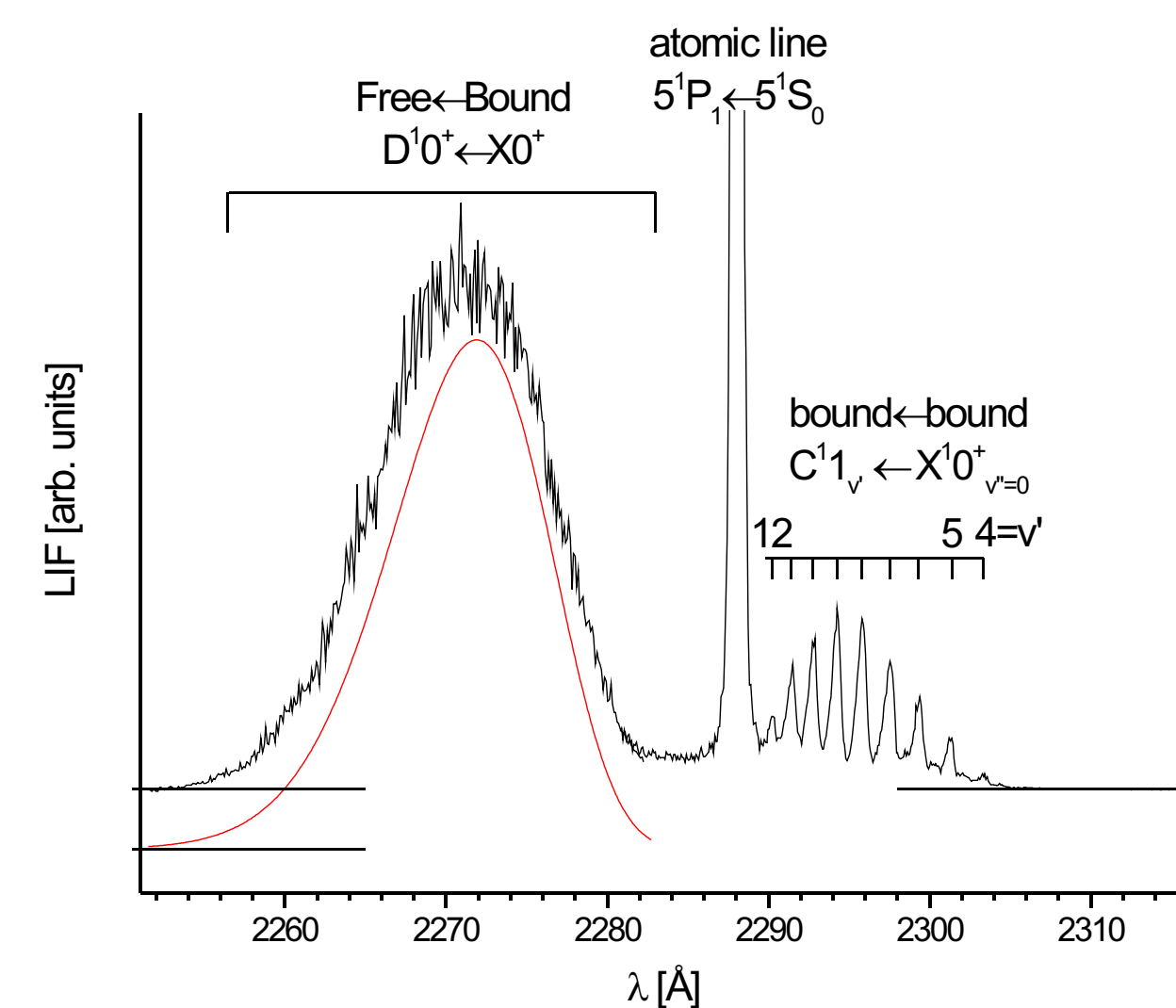


Fig. 3. Black line - D'0'←X'0' bound-free and C'1←X'0' bound-bound transitions in CdAr molecule recorded for D=200 μm, X=5 mm, p<sub>kr</sub>=13 Bar, and T=950 K. The vibrational assignment for the components in the C'1←X'0' transition is shown<sup>7,8</sup>. Red line - Simulation<sup>9</sup> of the bound-free profile using a Morse representations for the ground-<sup>9</sup> and excited-state potentials.

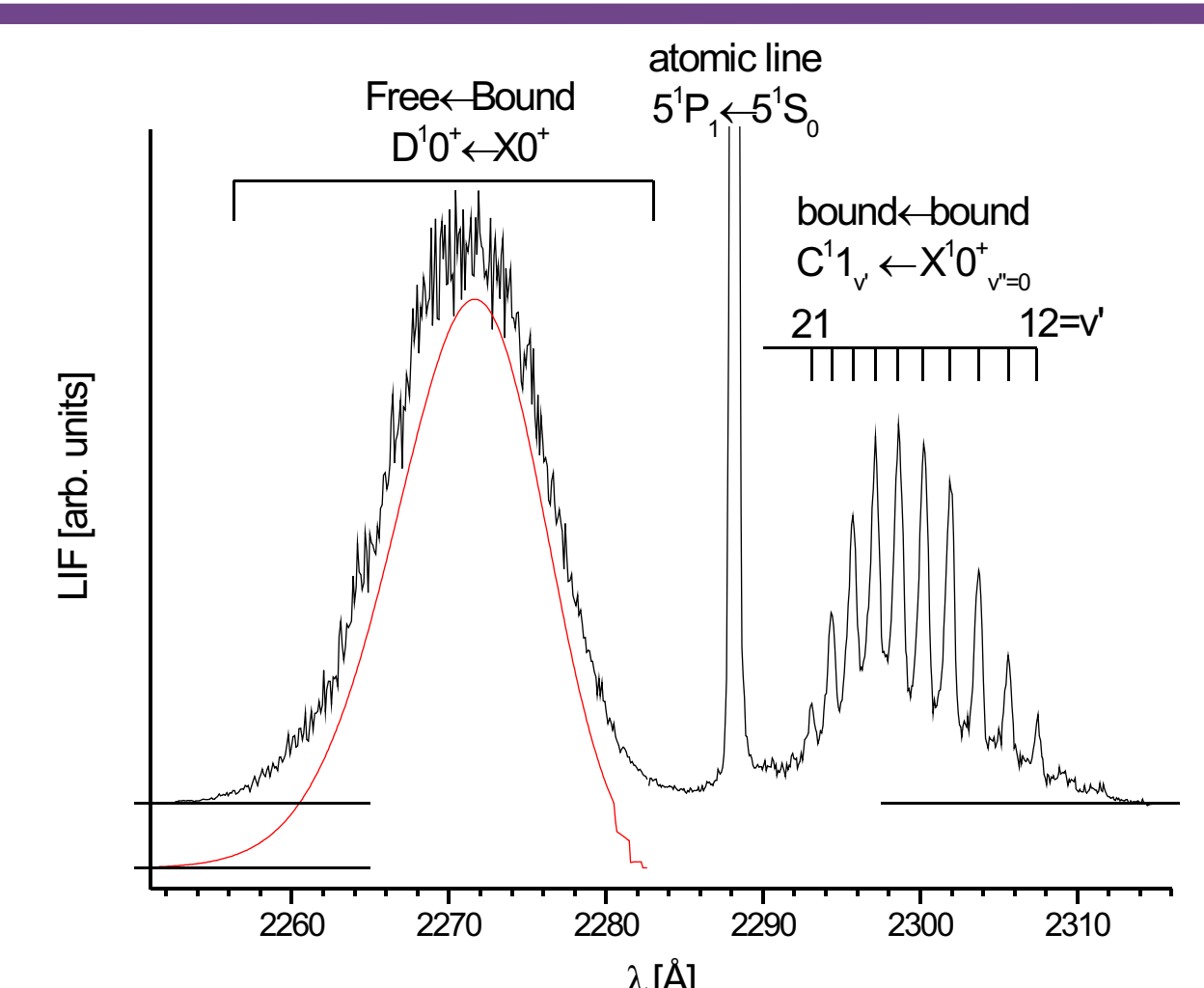


Fig. 5. Black line - D'0'←X'0' bound-free and C'1←X'0' bound-bound transitions in CdKr molecule recorded for D=200 μm, X=5 mm, p<sub>kr</sub>=13 Bar, and T=950 K. The vibrational assignment for the components in the C'1←X'0' transition is shown<sup>9</sup>. Red line - Simulation<sup>9</sup> of the bound-free profile using a Morse representations for the ground-<sup>9</sup> and excited-state potentials.

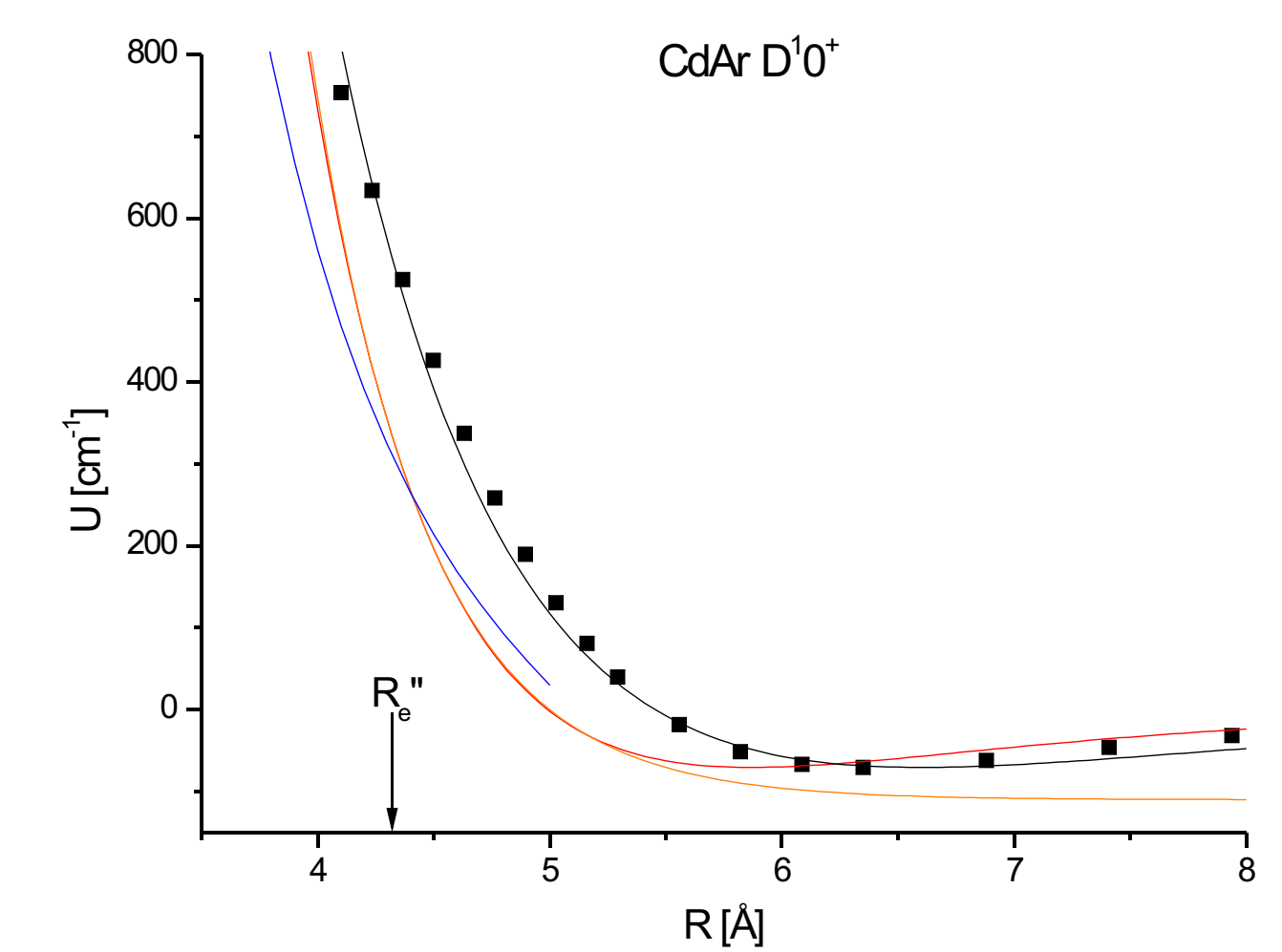


Fig. 4. D'0'-state interatomic potentials of the CdAr molecule. Buckingham-type potential of Funk *et al.*<sup>3</sup> (blue line); *ab initio* points of Czuchaj and Stoll<sup>6</sup> (full squares); Morse function fitted to the *ab initio* points (black line); A<sub>e</sub><sup>3R</sup>-C<sub>0</sub> Born-Mayer potential of this work (A=3.337×10<sup>2</sup> cm<sup>-1</sup>, b=1.575 Å<sup>-1</sup>, C<sub>0</sub>=110 cm<sup>-1</sup>, orange line); Morse potential of this work (D<sub>e</sub>'=70.5 cm<sup>-1</sup>, R<sub>e</sub>'=6.23 Å, β=0.6041 Å<sup>-1</sup>, red line). Position of the R<sub>e</sub>' is indicated.

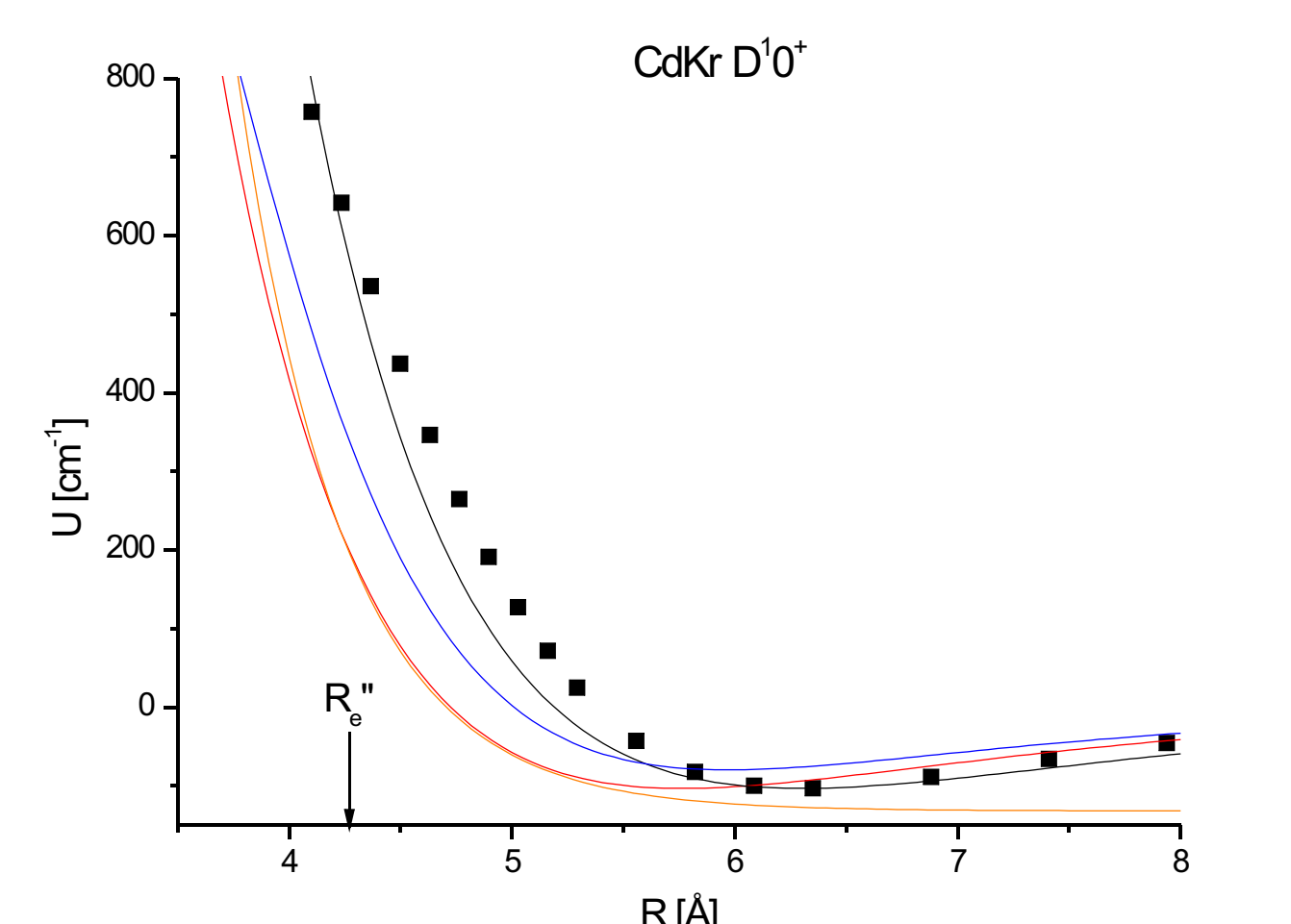


Fig. 6. D'0'-state interatomic potentials of the CdKr molecule. Buckingham-type potential of Funk *et al.*<sup>10</sup> (blue line); *ab initio* points of Czuchaj and Stoll<sup>6</sup> (full squares); Morse function fitted to the *ab initio* points (black line); A<sub>e</sub><sup>3R</sup>-C<sub>0</sub> Born-Mayer potential of this work (A=2.4852×10<sup>2</sup> cm<sup>-1</sup>, b=2.092 Å<sup>-1</sup>, C<sub>0</sub>=132 cm<sup>-1</sup>, orange line); Morse potential of this work (D<sub>e</sub>'=103.3 cm<sup>-1</sup>, R<sub>e</sub>'=5.76 Å, β=0.6670 Å<sup>-1</sup>, red line). Position of the R<sub>e</sub>' is indicated.

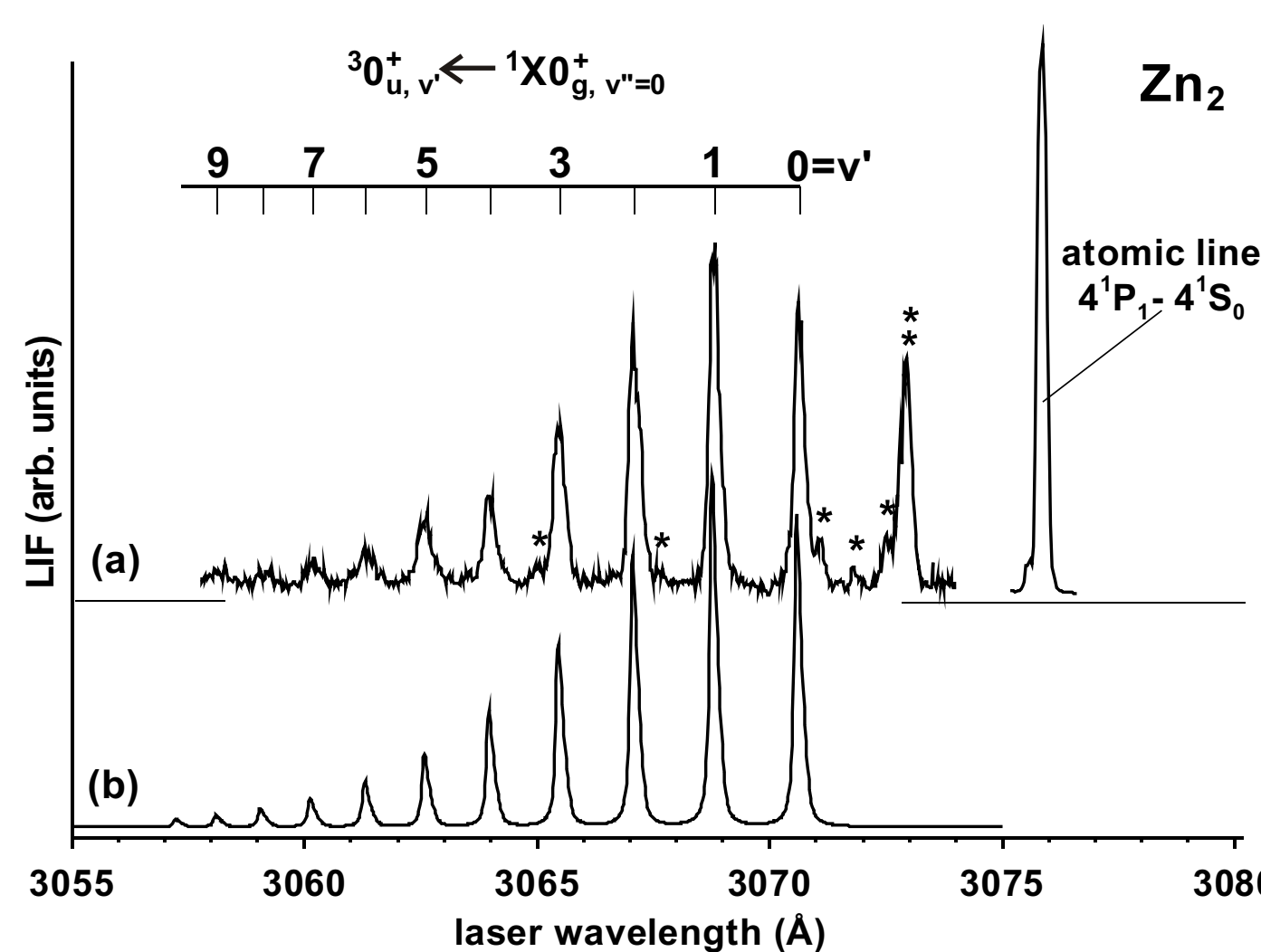


Fig. 8. (a) <sup>3</sup>0<sub>u</sub><sup>+</sup> (<sup>1</sup>Π<sub>u</sub>)←X'0<sub>g</sub><sup>+</sup> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) v'=0 bound-bound transitions in Zn<sub>2</sub> molecule recorded for D=200 μm, X=8 mm, p<sub>kr</sub>=7 Bar, and T=980 K. The vibrational assignment is shown. "Hot" bands and most probably ZnAr band are depicted with one and two asterisks, respectively. (b) Simulation<sup>12</sup> of the v'←v''=0 progression using Morse representations for the ground-state<sup>23</sup> and excited-state potentials. The rotational shading (B<sub>v</sub>'=0.0248 cm<sup>-1</sup> and B<sub>v</sub>''=0.0294 cm<sup>-1</sup>) was reconstructed for T<sub>rot</sub>=5 K and Lorentzian convolution (FWHM=1 cm<sup>-1</sup>) representing the laser beam spectral profile.

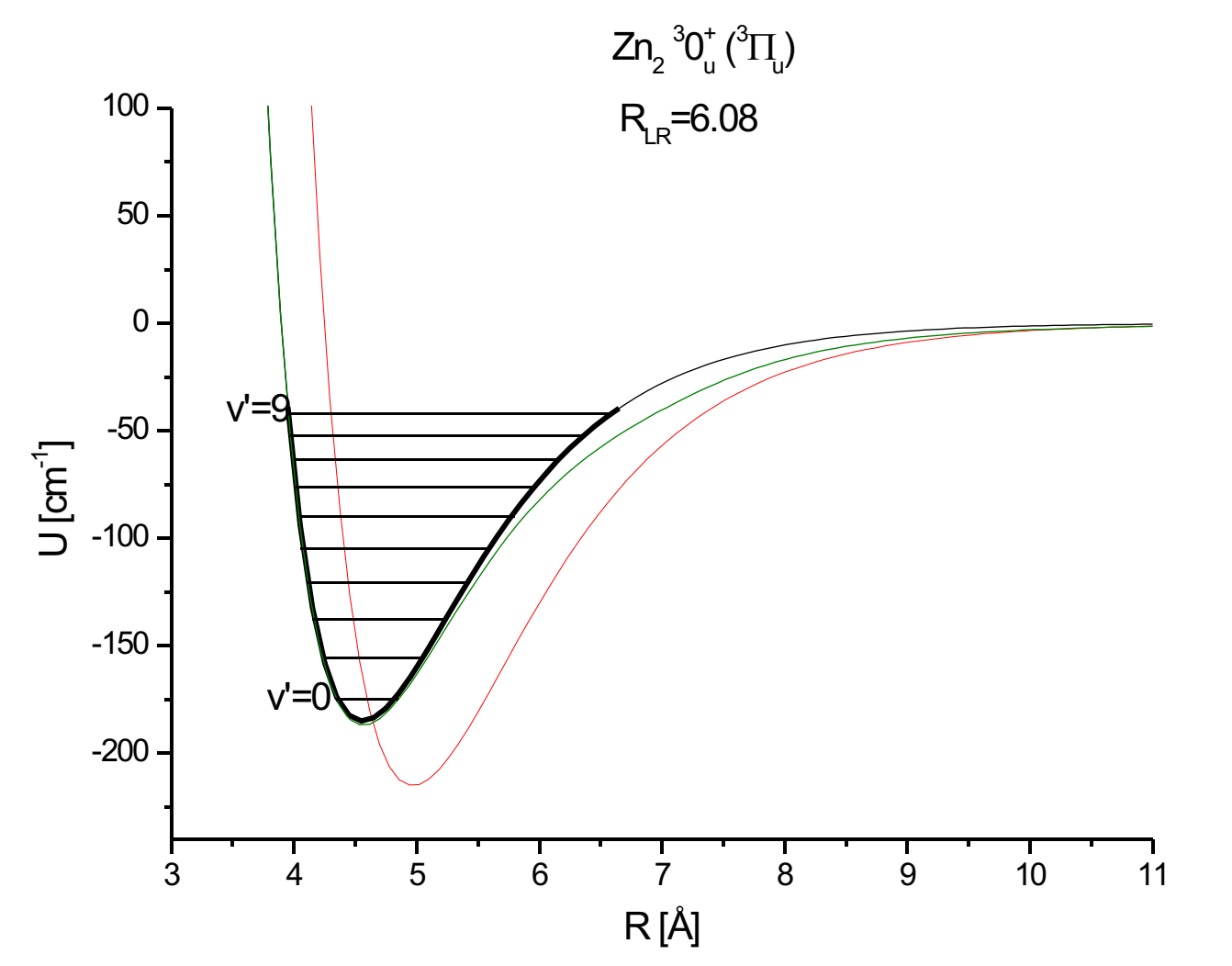


Fig. 9. <sup>3</sup>0<sub>u</sub><sup>+</sup> (<sup>1</sup>Π<sub>u</sub>)-state interatomic potentials of the Zn<sub>2</sub> molecule. Red line: Morse potential of Czajkowski *et al.*<sup>13</sup>; D<sub>e</sub>'=215 cm<sup>-1</sup>, R<sub>e</sub>'=4.97 Å, β=0.955 Å<sup>-1</sup>, ω<sub>e</sub>' x<sub>e</sub>'=0.47 cm<sup>-1</sup>, ω<sub>e</sub>'=20.1 cm<sup>-1</sup>. Black line: Morse potential of this work: D<sub>e</sub>'=185 cm<sup>-1</sup>, R<sub>e</sub>'=4.56 Å, β=1.044 Å<sup>-1</sup>, ω<sub>e</sub>' x<sub>e</sub>'=0.56 cm<sup>-1</sup>, ω<sub>e</sub>'=20.4 cm<sup>-1</sup>. Positions of detected vibrational levels (v'=0-9) are indicated. Thick black line: the part of the potential well "probed" in the experiment. Green line: Morse-vdW potential proposed by York *et al.*<sup>14</sup>.  
 $U_{Morse-vdW}(R) = D_e [(1 - e^{-B(R-R_e)})^2 - 1] - (1 - e^{-B(R-R_e)})^2 \times C_0 / R^6$   
Morse potential of this work combined with long-range potential of Ellingsen *et al.*<sup>15</sup>.