Vibrational spectra of the $E^3\Sigma^+_{1\ in}(6^3S_1)\leftarrow A^3\Pi_{0^+}(5^3P_1)$ transition in CdAr van der Waals complex studied using pulsed supersonic beam source method

Molecular Spectroscopy and Quantum Information

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Introduction

An optical-optical double resonance method (OODR) was used to excite the $E^3\Sigma_1^+{}_{in}(6^3S_1)$ lower-lying Rydberg state in CdAr van der Waals (vdW) complex, produced using a high-temperature pulsed supersonic source of molecular beam [1]. As an intermediaate, the $A^3\Pi_{0+}(5^3P_1)$ electronic state was employed. In Figure1 we present results of the measurements of vibrational energies of almost all vibrational components of the $E^3\Sigma_1^+{}_{in}\leftarrow A^3\Pi_{0+}(\upsilon''=5)$ transition (except of the $\upsilon'=0\leftarrow\upsilon''=5$). Figure 2 presents a Birge Sponer (B-S) plot with clearly visible signifficant nonlinearity for higher vibrational components. This indicates that the potential of the $E^3\Sigma_1^+{}_{in}$ state cannot be represented with the help of a Morse function representation (compare with [2]).

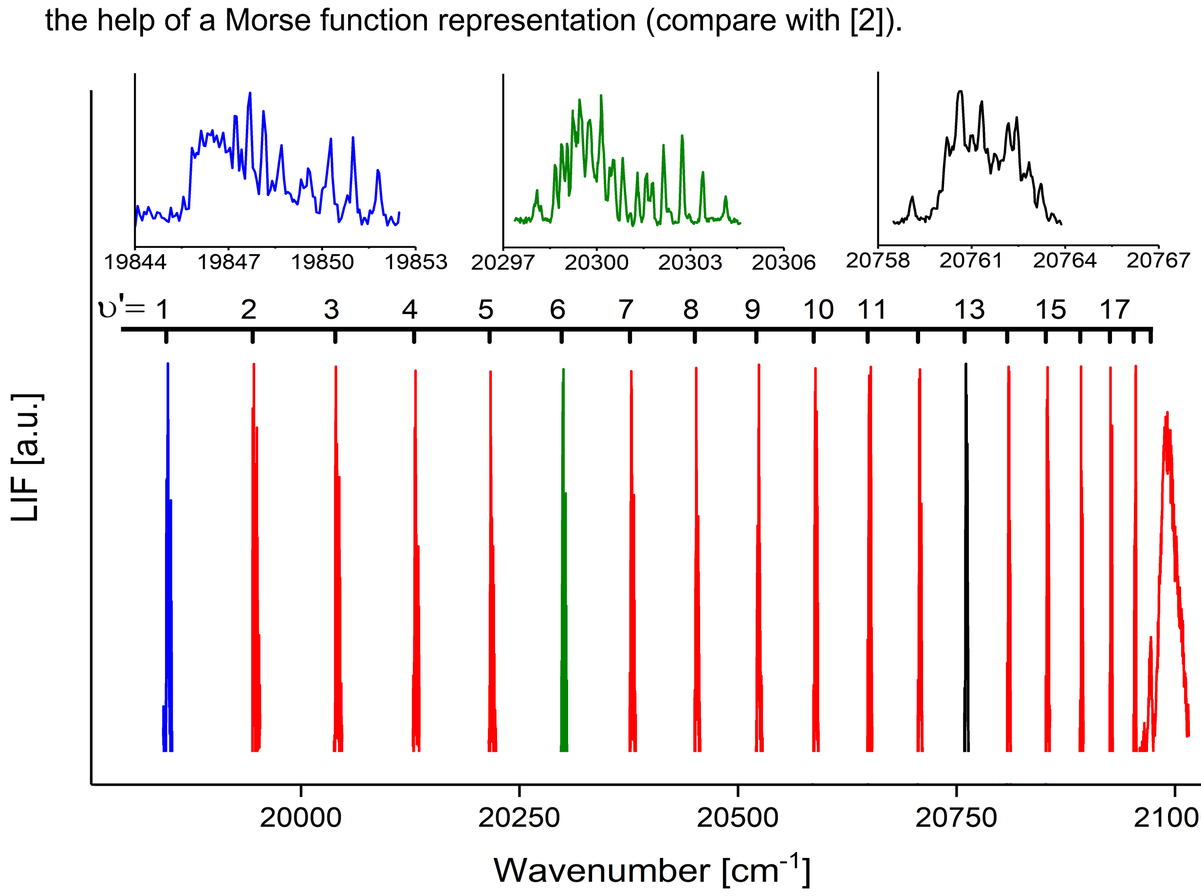

Figure 1. Experimentally observed components of the $E^3\Sigma_1^+{}_{in}\leftarrow A^3\Pi_{0+}(\upsilon''=5)$ transition in CdAr. Energy of all components were precisely measured using a wavemeter (High Finese WSU300). The intensities of all components were normalised. Three insets above: details of the $\upsilon'=1$, $\upsilon'=6$ and $\upsilon'=13$ components are presented. All components in the spectrum were measured independently.

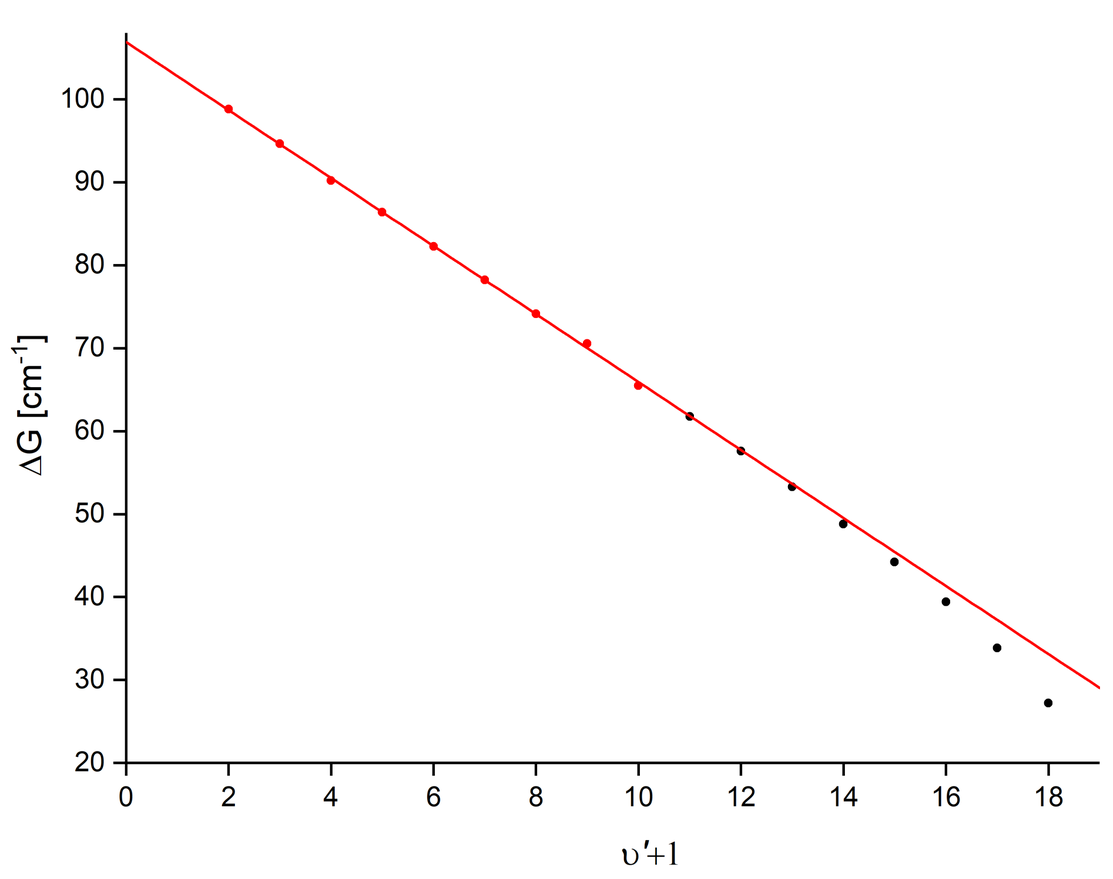

Figure 2. Nonlinearity in a B-S plot for the $E^3\Sigma_1^+{}_{in}\leftarrow A^3\Pi_{0+}(\upsilon''=5)$ transition in CdAr. Red line – linear interpolation obtained for experimental results shown with red points (for $\upsilon'<10$). Black points – remaining experimental results from the region of nonlinearity of the plot. Vibrational constants obtained by fitting linear function to the red points: $\omega_e' = 106.9\ cm^{-1}$, $\omega_e' x_e' = 2.049\ cm^{-1}$.

Estimation of parameters of the $E^3\Sigma_1^+{}_{in}$ - state interatomic potential

The blue trace (a) in Figure 3 shows a simulation of the experimental spectrum (red trace (c)) performed for a Morse representation of the $E^3\Sigma_1^+{}_{in}$ - state interatomic potential of CdAr (compare with Figure2). As one can see, there exist discrepancies between the simulated and experimental spectra. To find the representation of the $E^3\Sigma_1^+{}_{in}$ - state potential which ensures better simulation of the experimental spectrum, an inverted perturbation approach (IPA) method was employed. Black trace (b) in the Figure 3 presents simulation performed for the potential being the result of the IPA method (see red points and line in Figure 4 and data in Table 1).

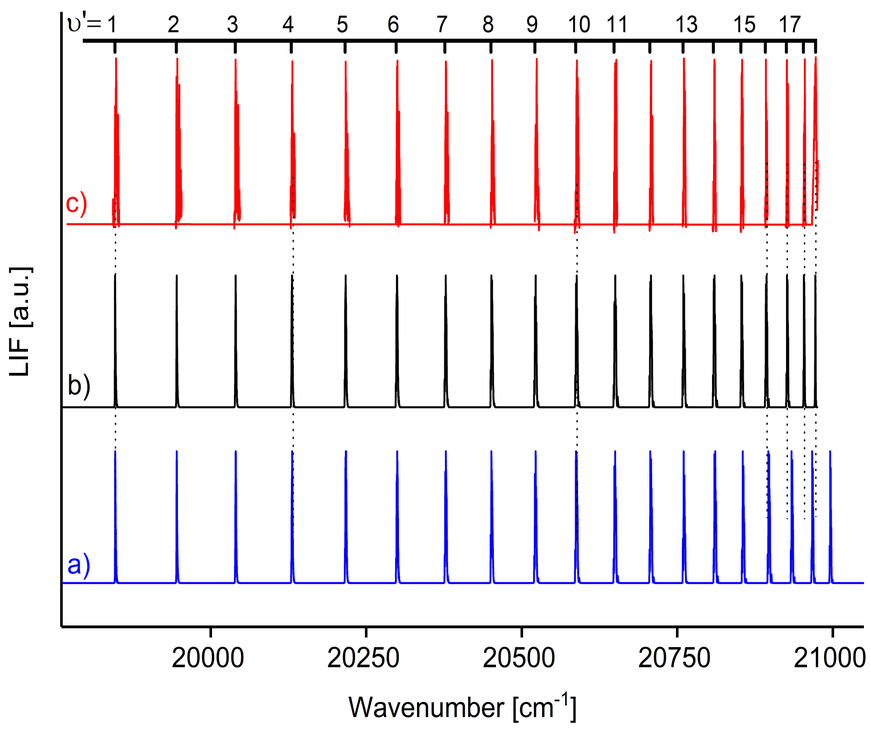

Figure 3. Experimental spectrum (red trace (c)) of the $E^3\Sigma_1^+{}_{in}\leftarrow A^3\Pi_{0+}(\upsilon''=5)$ transition in CdAr complex and its simulation (black trace (b)) performed using representation of the $E^3\Sigma_1^+{}_{in}$ state obtained from IPA method. The blue trace (c) shows simulation persormed using a Morse representation for the $E^3\Sigma_1^+{}_{in}$ state. The simulations were made using Level and Pgohper programs. For the experimental spectrum as well as for both simulations intensities of vibrational components were normalized.

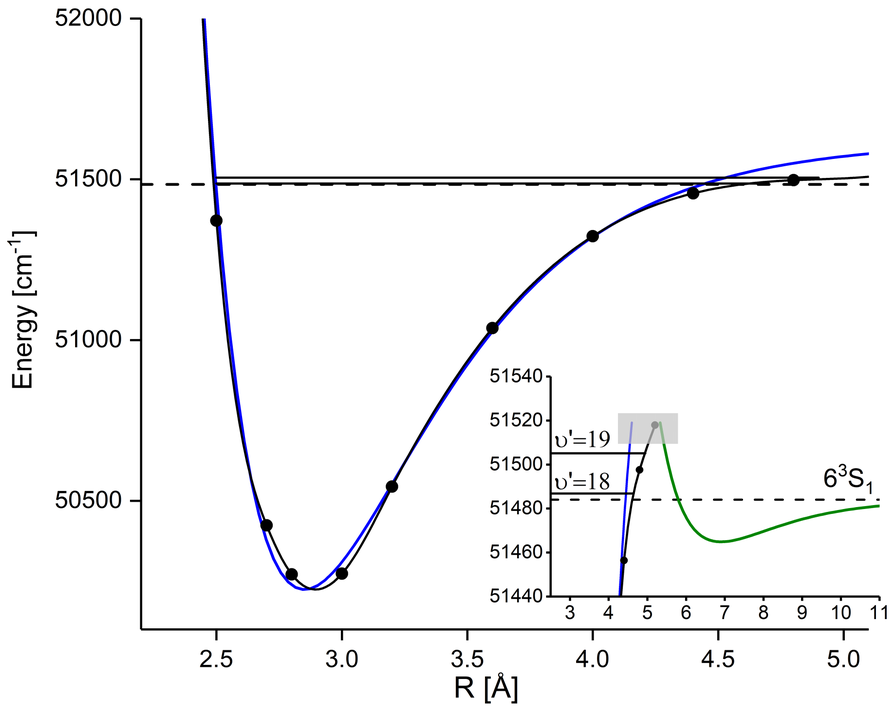

Figure 4. Representations of interatomic potential of the $E^3\Sigma_1^+{}_{in}$ electronic state in CdAr complex. Blue trace shows a Morse function with parameters $D_e' = 1394.29\ cm^{-1}$, $\beta' = 1.8962\ Å^{-1}$ corresponding to the vibrational constants $\omega_e' = 106.9\ cm^{-1}$, $\omega_e' x_e' = 2.049\ cm^{-1}$ obtained using a B-S plot (see Fig. 2) and the equilibrium distance $R_e' = 2.85$ Å. Black points and line show result of IPA method. Compare with simulations of the experimental spectrum shown in Fig. 3. The 6^3S_1 asymptote is shown with dashed horizontal line. Black solid horizontal lines: positions of the $\upsilon'=18$, 19 levels that lie above the asymptote due to existence of a potential barrier and second shallow potential well with $R_e' = 6.9$ Å [3] (see green trace in inset). Grey rectangle depicts region of the potential barrier.

R [Å]	Energy [cm^{-1}]
1.3	496985.79
1.4	348885.53
1.5	248830.26
1.6	181431.10
1.7	136194.23
1.9	85901.64
2.1	64016.99
2.3	54963.11
2.5	51371.31
2.7	50423.63
2.8	50271.38
3.0	50273.70
3.2	50544.41
3.6	51037.06
4	51322.81
4.4	51456.42
4.8	51497.58
5.2	51517.89
5.4	51551.61

Table 1. Potential of the $E^3\Sigma_1^+{}_{in}$ state in CdAr complex obtained using IPA method. Compare with red trace (c) in Figure 4.

Acknowledgements

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References

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[3] T. Urbanczyk, J. Koperski, *Chem. Phys. Lett.* **640** (2015), 82-86.