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High Temperature Pulsed Valve and Its Application to Laser Spectroscopic Study of CdAr van der Waals Complex

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A high temperature pulsed valve which can be operated at temperatures up to 600 °C is developed and applied to laser spectroscopy of CdAr van der Waals complex. On the basis of rotational analysis of the laser induced fluorescence spectra of the C-X transitions, the interatomic potential of the C state of CdAr is determined.

In the last decade, geometrical structures and dynamical properties of van der Waals (vdW) complexes formed in supersonic jets were extensively studied by laser spectroscopy. A pulsed valve is now widely utilized to produce the vdW complexes in supersonic jets. Among the vdW complexes, metal-rare gas[1-5)] and metal-molecule[6,7)] complexes are of significance for detailed discussion of the photochemical reaction as well as the quenching process associated with the electronically excited metal atom. For most of the metal-vdW complexes metal vapor pressure below 300 °C is not enough to form the detectable concentration of the complexes in the jet and thus a heated continuous nozzle[1,4,5)] was introduced since the commonly used pulsed valve cannot be operated above 300 °C.[8)] The pulsed valve was applicable for formation of only Hg-rare gas [2,3)] and Hg-molecule[4,5)] complexes. In the present study, in order to produce efficiently cooled metal vdW complexes with a relatively small pumping facility, a high temperature pulsed valve which can be operated at a temperature higher than 500 °C is developed and its operation is demonstrated by measurement of the laser induced fluorescence (LIF) spectra of the C-X transitions of CdAr vdW complex.

A schematic diagram of a high temperature pulsed valve developed in the present study is shown in Fig. 1. The nozzle tip and the sample reservoir are separately heated by two sheathed nichrome wire heaters (200 W). The nozzle temperature is kept higher than the reservoir temperature by 50-100 °C in order to avoid aggregation of metal deposit at the nozzle orifice. The pulsed valve is made of stainless steel (SUS304) except for the water-cooled copper block, iron plunger, and copper gasket. The solenoid coil is cooled by a water-circulated copper block. The stem of the plunger (10 cm long) made of iron steel is connected to the plunger head which is used in a commercial fuel injector. In order to avoid gas leakage, a copper gasket is employed. The highest temperature of the reser-

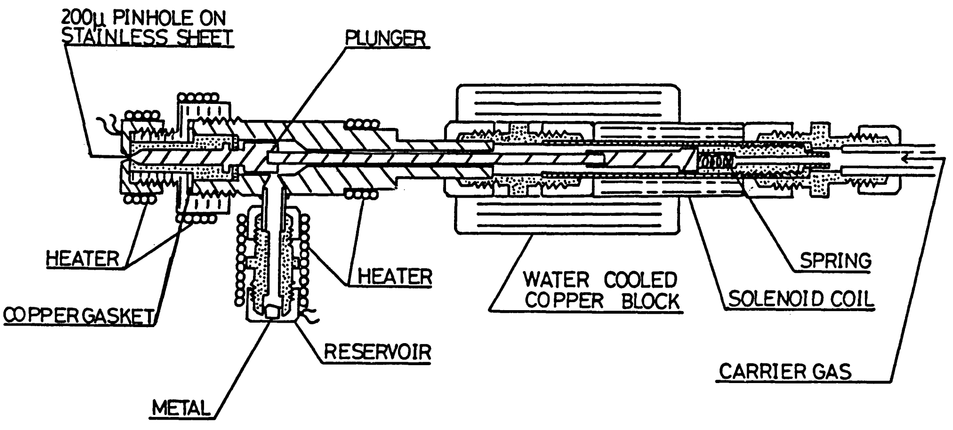

Fig. 1. A schematic diagram of the high temperature pulsed valve developed in the present study.

voir achieved by the present setup is 600 °C. A typical pulsed current applied to the solenoid coil (about 700 turns and 50 mm long) is 2-4 A and the pulse width is 2-3 ms. The FWHM of pulse width of the jet, which is measured by the LIF intensities of CdAr complex as a function of the delay time from the trigger pulse, is about 1 ms when the stagnation pressure is 3.2 atm. The pulse width can be controlled by the strength of the spring and the pulsed current. In a stable operation, the back ground pressure in the vacuum chamber is $1\text{-}2\times10^{-4}$ Torr at a stagnation pressure of 3-4 atm when the nozzle orifice diameter is 0.2 mm.

In order to produce the CdAr vdW complex in a supersonic jet, pure Ar gas with Cd vapor is expanded into the vacuum chamber through the high temperature pulsed valve with a stagnation pressure of 4 atm at a repetition rate of 10 Hz. The reservoir temperature is 400 °C which corresponds to about 1 Torr of Cd vapor pressure. The free jet is crossed by the frequency-doubled output of a dye laser (Lambda Physik FL 3002) pumped by a XeCl Excimer Laser (Lambda Physik LPX 105) at 15 mm downstream from the nozzle orifice. The fluorescence signal detected by a solar-blind photomultiplier (Hamamatsu R166UH) is amplified by a preamplifier (Brookdeal 9495), and then averaged by a boxcar integrator (Stanford SR250). The vacuum chamber is evacuated by two 14 inch diffusion pumps with a water-cooled baffle, which are backed up separately by a mechanical booster pump and a rotary pump. When the dye laser is grating-tuned, the wavenumber resolution is 0.5 cm^{-1} and it is improved to be 0.05 cm^{-1} with an intracavity etalon. The laser beam is partially split for its intensity monitor as well as for the measurement of absorption spectra of Te_2 to calibrate the laser wavelength. The intensities of the LIF spectrum of CdAr is normalized by the laser intensities. The accuracy of the transition wavenumbers in the high resolution measurements is 0.02 cm^{-1}.

The LIF spectrum of the C-X transitions of CdAr vdW complex is measured as shown in Fig. 2. One vibronic band system with eleven peaks in the red side of Cd ($^1P_1$-$^1S_0$) atomic resonance line located at 228.8 nm is observed. The assignment of the vibrational quantum number v' is performed based on the isotope splittings derived from their rotational contour analysis. The high resolution spectra of the five vibronic transitions, v'=5-9 in the C-X transitions, are shown in Fig. 3. The blue-shaded structures of these spectra indicate that the interatomic distance of the C state is shorter than that of the ground state. These complicated rota-

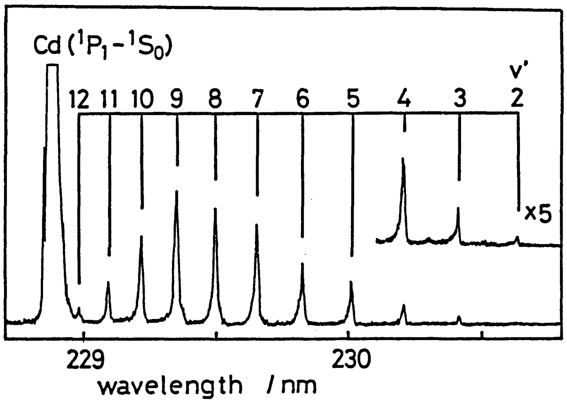

Fig. 2. Low resolution spectra of the C-X transitions of CdAr vdW complex.

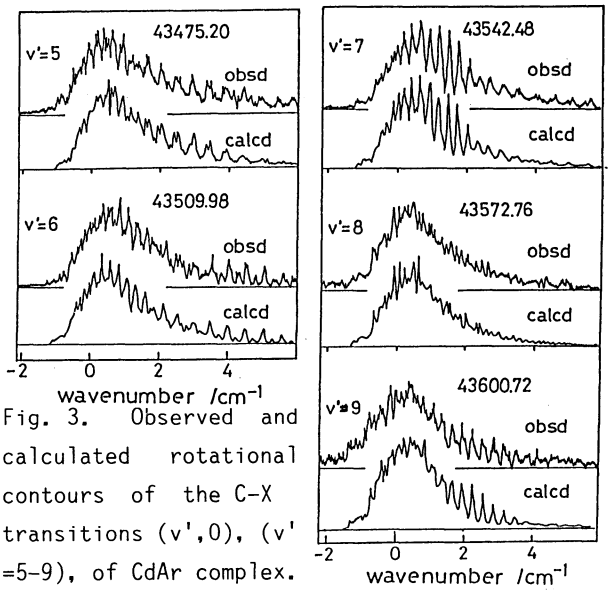

Fig. 3. Observed and calculated rotational contours of the C-X transitions (v',0), (v'=5-9), of CdAr complex. Band origine in cm^{-1} is denoted in each frame. T_R=4.3 K.

tional structures are analyzed by the same method as described in our previous report.$^{2)}$

In the simulation of these spectra, the six rotational structures for respective isotope species ^{m}CdAr (m=110, 111, 112, 113, 114, and 116) are added with their weights proportional to the natural abundances using calculated isotope shifts. The isotope splitting between the band origins of two isotope species ^{i}CdAr and ^{j}CdAr in the C-X (v',0) transition, is expressed$^{2)}$ as

$$\Delta_{iso}(v',i,j)=(1-\rho)\omega_e(v'+1/2)-(1-\rho^2)\omega_e x_e(v'+1/2)^2+\delta \qquad (1)$$

where ω_e and $\omega_e x_e$ are Morse parameters, $\rho=\sqrt{\mu(i)/\mu(j)}$, $\mu(i)$ is the reduced mass for ^{i}CdAr, and δ is a contribution of the vibrational isotope splitting in the ground state, which can be calculated by the potential parameters in Table 3. Since the isotope splittings in the Cd($^1P_1$-$^1S_0$) atomic line$^{9)}$ are negligible in the present resolution, the contribution of the nuclear volume effect$^{2)}$ is disregarded. For the three transitions which are to be assigned to the (5,0), (7,0), and (9,0) transitions, the P-branch heads of the ^{116}CdAr and ^{114}CdAr are clearly identified in the high resolution spectra as shown in Fig. 3. Regarding the difference between these bandheads as the isotope shifts of their band origins, the assignment of v' is performed by comparison with the calculated isotope shifts.

Using three independent parameters B'_v, B''_0, and T_R, observed rotational structures are simulated by a trial and error method. The optimized parameters are listed in Table 1. The existence of the Q-branch transitions in the observed rotational spectra indicates that Ω is 1 for the C state (in Hunt's case (c) representation). The vibronic assignment as ^{1}1 for the C state is consistent with that predicted by a theoretical calculation.$^{10)}$

On the basis of ω_e and $\omega_e x_e$ derived from the Birge-Sponer's plot the dissociation energy D_e is calculated assuming the Morse potential. The equilibrium interatomic distances r'_e and r''_e for the Morse potential are adjusted so that the squared sum of the differences between the observed and calculated rotational constants is minimized. The determined potential parameters are summarized in Table 2.

The equilibrium interatomic distances r_e and the dissociation energies D_e of the X $^1 0^+$ and C $^1 1$ states of CdAr complex are compared with those of HgAr in Table 2. In the case of the X $^1 0^+$ state, the r_e for the CdAr is longer than that for the HgAr by 0.35 Å and the D_e for the CdAr is 25% smaller than that for the HgAr. However, in the C $^1 1$ state, the r_e and D_e for CdAr are almost the same as those for HgAr within the experimental errors. Recently Funk et al.$^{5)}$ have observed the LIF and dispersed fluorescence spectra of the C-X transitions of Cd-rare gas complexes by a conventional continuous nozzle, and their results on the C state potential and the vibrational assignment of v' of CdAr are consistent with the present results.

Table 1. Rotational constants (cm^{-1}) and bond lengths (Å) for the X and C states of CdAr

	v	B_v /cm^{-1}	r_v /Å
X $^1 0^+$	0	0.0302	4.35(4)
C $^1 1$	5	0.0459	3.53(6)
	6	0.0444	3.59(6)
	7	0.0427	3.66(6)
	8	0.0409	3.74(6)
	9	0.0392	3.82(6)

Table 2. Potential parameters for the X and C states of CdAr and HgAr complexes

		CdAr		HgAr	
		X $^1 0^+$	C $^1 1$	X $^1 0^+$	C $^1 1$
ω_e	/cm^{-1}	$20^{a)}$	48.2	$23.5^{b)}$	$50.3^{c)}$
$\omega_e x_e$	/cm^{-1}	$1.0^{a)}$	1.12	$1.06^{b)}$	$1.29^{c)}$
D_e	/cm^{-1}	$106^{a)}$	518	$142^{b)}$	$487^{c)}$
r_e	/Å	4.34	3.27	$3.99^{b)}$	$3.28^{c)}$

a) Ref. 4. b) Ref. 2. c) Ref. 3.

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References

1)e.g., E.Zanger, V.Schmatloch, and D.Zimmermann, J. Chem. Phys., 88, 5396 (1988).

2)e.g., K.Yamanouchi, S.Isogai, M.Okunishi, and S.Tsuchiya, J. Chem. Phys., 88, 205 (1988).

3)T.Tsuchizawa, K.Yamanouchi, and S.Tsuchiya, J. Chem. Phys., 89, 4646 (1988).

4)A.Kowalski, M.Czajkowski, and W.H.Breckenridge, Chem. Phys. Lett., 121, 217 (1985); A.Kvaran, D.J.Funk, A.Kowalski, and W.H.Breckenridge, J. Chem. Phys. in press.

5)D.J.Funk, A.Kvaran, and W.H.Breckenridge, J. Chem. Phys., in press.

6)K.Yamanouchi, S.Isogai, S.Tsuchiya, M.C.Duval, C.Jouvet, O.B.d'Azy, and B.Soep, J. Chem. Phys., 89, 2975 (1988).

7)K.Fuke, T.Saito, S.Nonose, and K.Kaya, J. Chem. Phys., 86, 4745 (1987).

8)M.Fujii, T.Tamura, N.Mikami, and M.Ito, Chem. Phys. Lett., 126, 583 (1986).

9)F.M.Kelly and E.Tomchuk, Proc. Phys. Soc., 78,1304 (1961).

10)E.Czuchaj and J.Sienkiewicz, J. Phys. B, 17, 2251 (1984).

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