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# Spectrophotometric and Raman Spectroscopic Studies of the Palladium(II) Bromide–Aluminum(III) Bromide Vapor Complex

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The reaction of solid palladium(II) bromide with gaseous aluminum(III) bromide to form a ceramic-red vapor complex has been investigated by spectrophotometry and by Raman spectroscopy at temperatures ranging from 550 to 900 K and total pressures up to ~2 atm. The electronic absorption spectra of the complexes show an intense d → d band at ~1.96 $\mu m^{-1}$ and a charge-transfer band at ~3.55 $\mu m^{-1}$. The spectrophotometric data led to the conclusion that one predominant complex exists in the vapor formed by the reaction $PdBr_2(s) + Al_2Br_6(g) \rightleftarrows PdAl_2Br_8(g)$ with $\Delta H = 8.27$ kcal/mol and $\Delta S = 8.04$ eu. Raman spectra of the equilibrium vapor mixtures $PdAl_2Br_8$–$Al_2Br_6$–$AlBr_3$ and $Al_2Br_6$–$AlBr_3$ were obtained at different temperatures. The main features of the Raman spectra of the $PdAl_2Br_8$ gaseous molecule are three polarized bands at 180, 114, and ~50 $cm^{-1}$. The excitation profiles of these bands exhibit minima in the vicinity of the maximum Pd(II) d → d absorption. The electronic absorption and Raman spectra of the complex were interpreted in terms of a $D_{2h}$ symmetry for the vapor complex $PdAl_2Br_8$, where Pd(II) is in a square-planar coordination.

## Introduction

In recent years, spectrophotometric, mass spectrometric, and gas transpiration studies have established the existence of vapor complexes at temperatures between 500 and 1000 K formed by the reactions

$$mMX_2(s) + nA_2X_6(g) \rightleftarrows M_mA_{2n}X_{6n+2m}(g) \qquad (1)$$

where M is transition metal, A = Al,[2-7] Ga,[8] or In,[9,10] and X is either Cl[2,3,5-8] or Br.[4] With X = Cl, the most recently studied transition metals have been Cu,[11] Co,[3] V,[5] and Cr.[12] In all cases studied it was found that $n = 1$, while the value of $m$ was assumed to be 1. Mass spectrometric studies on these vapor complexes support the assumption that $m = 1$ for all the chlorides studied.[6]

Since the transition metals in these vapor complexes are ligand field sensitive, some information on the structure of the complexes can be extracted from the spectrophotometric data. In the majority of cases, however, interpretation of the electronic absorption spectrum in terms of the configuration of the metal ligands is ambiguous. Additional vibrational studies on these vapor complexes are necessary to obtain more conclusive knowledge on their possible structure. To date, only the vapor complexes $PdAl_2Cl_8$[13] and $CuAl_2Cl_8$[13,14] have been investigated by Raman spectroscopy.

In the first part of this work, the reaction

$$mPdBr_2(s) + nAl_2Br_6(g) \rightleftarrows Pd_mAl_{2n}Br_{6n+2m}(g) \qquad (2)$$

was studied spectrophotometrically and the thermodynamics of formation and the stoichiometry were determined in the temperature range from 550 to 750 K and at total pressures up to ~2 atm. In the second part of this work, the equilibrium vapor species formed according to reaction 2 were investigated by Raman spectroscopy in order to obtain information on the vibrational modes and structure of the vapor complex.

## Experimental Section

The $AlBr_3$ was obtained from Cerac Pure, Inc., and purified by several slow sublimations in evacuated glass tubes. The palladium(II) bromide was purchased from Matheson Coleman and Bell and purified by vapor transport in an evacuated tube to which small amounts of $AlBr_3$ had been added. The salts were handled in a helium-atmosphere drybox with a water vapor content of less than 30 ppm. The salts were placed in fused-silica cells which had been thoroughly cleaned and degassed. The cells were then sealed under vacuum. Cell volumes ranged from 5 to 30 mL and were calibrated to within 1%.

The light absorption experiments were performed on a Cary 17H spectrophotometer which had been equipped with a high-temperature cell compartment. The optical cells for the absorption experiments were fused-silica UV-type cylindrical cells having path lengths of 2, 5, and 10 cm. To avoid condensation of excess solid palladium bromide on the cell windows, the temperature gradients of the spectrophotometer cell compartment were adjusted to keep the windows 2–3 K hotter than the center of the cell.

Cells which had no excess $PdBr_2$ solid were prepared by equilibrating the solid with aluminum bromide at temperatures of 540–600 K. The vapors were then condensed by quickly cooling the cell, leaving the excess solid in the cell's side tube. The side tube was finally sealed off. For the absorptivity measurements, the unknown quantity of $PdBr_2$ thus transported in the cell was later determined to within 1% by chemical analysis.

Cells with excess $PdBr_2$ solid, used for equilibrium measurements, were prepared by introducing into each cell preweighed quantities of aluminum bromide and sufficient $PdBr_2$ to leave excess solid at the temperature and pressure studied.

The Raman spectra were excited by use of a CR-3 Coherent Radiation argon ion laser or a Coherent Radiation dye laser pumped with all $Ar^+$ laser lines. A Spex 1400 double monochromator equipped with a Channeltron phototube analyzed the scattered light at 90° from the incident laser beam. The Raman cells were 20-mm o.d., 18-mm i.d. fused-silica tubing sealed at both ends to lengths of 2.5–5 cm. The furnace used and the experimental procedures for obtaining the Raman spectra have been described elsewhere.[13,15,16]

## Results and Discussion

**Thermodynamics and Stoichiometry.** The electronic absorption spectrum of the Pd–Al–Br vapor complex(es) is given in Figure 1. In the 1.0–4.5-$\mu m^{-1}$ range the spectra exhibit two maxima, one at 1.96 $\mu m^{-1}$ and another at 35.5 $\mu m^{-1}$. To obtain the "apparent" molar aborptivities, $\epsilon$, five cells were prepared with no excess $PdBr_2$ solid. From the absorbance, $A$, of these cells, $\epsilon$ was derived by Beer's law, $\epsilon = AV/nl$, where $V$ is the volume of each cell, $n$ is the number of moles of $PdBr_2$ in the cell, and $l$ is the absorption path length. Table I[17] lists the "apparent" molar absorptivities obtained for the maximum at 1.96 $\mu m^{-1}$, $\epsilon_{max}$, at various temperatures and pressures of $Al_2Br_6$. It was found that within the calculated maximum experimental uncertainty of 3.3%, $\epsilon_{max}$ varied linearly with $T$:

$$\epsilon_{max} = 169.8 + 0.294T(\mathrm{K})\ \mathrm{L/(mol\ cm)} \qquad 550\ \mathrm{K} \le T \le 750\ \mathrm{K} \qquad (3)$$

Measurements at temperatures above 750 K showed that $\epsilon_{max}$ decreases rapidly with increasing temperature (Table I; experiments 4 and 5). This decrease in $\epsilon_{max}$ has also been observed for the vapors of the $CoCl_2$–$In_2Cl_6$ system and has been attributed[10a] to dissociation of the $CoIn_2Cl_8$ complex to lighter molecular weight vapor species [e.g., $CoInCl_5(g)$ and $CoCl_2(g)$]. For the Pd–Al–Br complexes further dissociation of the $PdBr_2$ vapors to Pd metal and to the low molar absorptivity $Br_2(g)$[10b] may also contribute to decreasing values of $\epsilon$. However, the data presented here are not adequate for a determination of the different species present at temperatures above 750 K.

Figure 1 shows that the frequency at which $\epsilon_{max}$ occurs shifts toward the red and the band broadens as the temperature is

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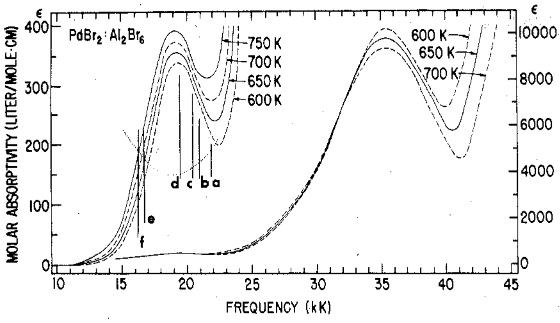

**Figure 1.** Molar absorptivity of the palladium(II) bromide–aluminum bromide vapor complex at different temperatures. Vertical lines indicate laser lines used to excite the Raman spectra: a, 457.9 nm; b, 476.5 nm; c, 488.0 nm; d, 514.5 nm; e, 596.8 nm; f, 611.3 nm. Dotted line is the excitation profile at 600 K of the 114-cm$^{-1}$ Raman band of PdAl$_2$Br$_8$.

increased in this range. This effect is similar to that observed in the PdAl$_2$Cl$_8$ vapor complex.[2] In the pressure range from ~0.4 to ~2 atm of Al$_2$Br$_6$ and $T \leq 750$ K, the molar absorptivity of the Pd–Al–Br complex(es) is independent of pressure (Table I). If we assume, however, as indicated by the studies of other systems,[1–9] that the gaseous complex(es) is mononuclear in Pd(II) (i.e., $m = 1$ in eq 2), then the pressure-independent molar absorptivity implies that there is one predominant palladium gaseous complex present and that is of the type PdBr$_2$·$n$Al$_2$Br$_6$.

The nature of the solid which exists in equilibrium with the vapor in eq 2 was studied. A small amount of PdBr$_2$ was placed at one end of an evacuated fused-silica tube containing aluminum bromide. The tube was heated and the PdBr$_2$ was vapor-transported to the other end of the tube at a temperature of ~650 K. The transported red-black solid was analyzed by X-ray diffraction and found to be $\gamma$-PdBr$_2$. This $\gamma$ form of PdBr$_2$ is known to exist up to 824 K, where it undergoes a transformation into the $\beta$ form.[18,19] The only known solid phases of PdBr$_2$ are given in the scheme

$$\gamma\text{-PdBr}_2 \xrightarrow{824\ \text{K}} \beta\text{-PdBr}_2 \xrightarrow{924\ \text{K}} \alpha\text{-PdBr}_2 \xrightarrow{1073\ \text{K}} \text{Pd} + \text{Br}_2$$

X-ray diffraction did not indicate any other substances present in the transported solid.

The value of $n$ for the vapor complex was determined from the equilibrium pressure experiments, where the absorbance of the complex was measured over excess solid PdBr$_2$(s) at various temperatures and Al$_2$Br$_6$ pressures. By varying the temperature of the cell it was found that equilibrium was reached in less than 5 min at temperatures above 600 K. The characteristics of these experiments are listed in Table II.[17] The apparent pressure, $P_c$, of the vapor complex was determined from the maximum absorbance $A_{\max}$ near 1.9 $\mu$m$^{-1}$ and the relation

$$P_c = A_{\max}RT/(\epsilon_{\max}l) \qquad (4)$$

where $R$ is the gas constant. The pressure $P'$ of the dimer, without consumption due to the formation of the complex, was calculated from the "ideal" gas pressure, $P_0$, of Al$_2$Br$_6$ calculated from the added moles of Al$_2$Br$_6$ in the cell and the equilibrium constant for the reaction[4]

$$\text{Al}_2\text{Br}_6(\text{g}) \rightleftarrows 2\text{AlBr}_3(\text{g}) \qquad (5)$$

The values of $P_c$ were found to be proportional to the Al$_2$Br$_6$ pressure $P'$ (Figure 2). This implies[2–4] that there is only one Al$_2$Br$_6$ molecule per complex molecule (i.e., $n = 1$ in eq 1) and that the predominant gaseous complex has the stoichiometry PdAl$_2$Br$_8$. With this stoichiometry, the thermodynamics of reaction 2 ($m = n = 1$) can be derived from Arrhenius plots.

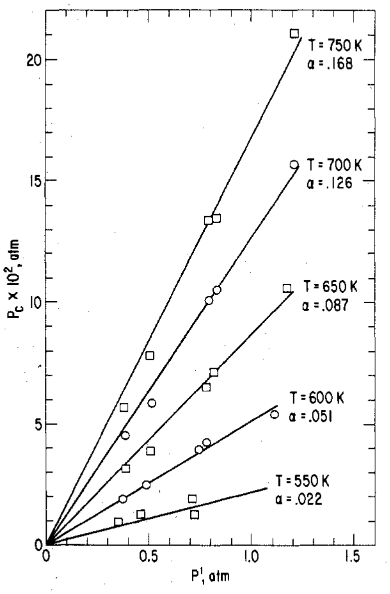

**Figure 2.** Plots of $P_c$ vs. $P'$ at different temperatures. The slopes $\alpha$ were determined by least-squares treatment of the data including the origin ($P' = 0$; $P_c = 0$).

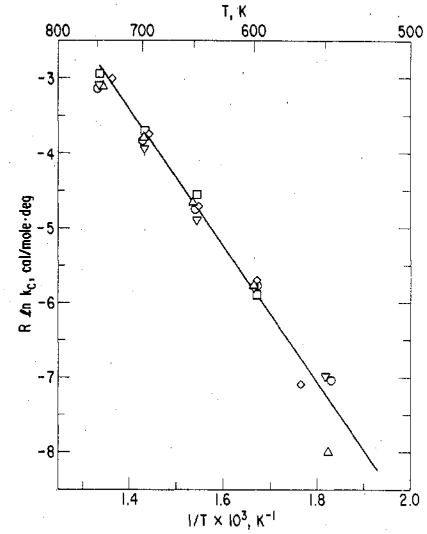

**Figure 3.** Plot of $R \ln k_c$ vs. $1/T$ for reaction B in Table III.

By taking into account the consumptions of the dimer due to reactions 2 and 5, the actual dimer pressure can be calculated from eq 4 and the mole balance equation

$$M_0 = M_D + 2M_m + M_c \qquad (6)$$

where $M_0$ is the number of moles of Al$_2$Br$_6$ introduced into the cell and $M_m$, $M_D$, and $M_c$ are, respectively, the number of moles of monomer, dimer, and gaseous complex formed according to reactions 2 and 5.

The values of $R \ln k_c$ for reaction 2 are plotted vs. $1/T$ in Figure 3. The apparent enthalpy and entropy according to the second law can be deduced from these figures; these values are listed in Table III. In the same table we list, for comparison, the thermodynamic quantities of the PdAl$_2$Cl$_8$ complex.

The similarity of the thermodynamics of formation of reactions A and B in Table III suggests that the structures of the chloride and bromide complexes are similar.[4] The ~1.5 kcal/mol difference in the enthalpies of formation is attributed to the stronger bonding exhibited by the chloride, relative to the bromide, in these complexes. Furthermore, reaction 5 is more endothermic than the dissociation Al$_2$Cl$_6$(g) $\rightleftarrows$ 2AlCl$_3$(g) and this, according to the models described by Hastie[20] and

**Table III.** Thermodynamic Quantities for Palladium Halide-Aluminum Halide Gas-Solid Reactions

| reaction | $\Delta H$,[a] kcal/mol | $\Delta S$,[a] eu | temp range, K |
|---|---|---|---|
| (A) $PdBr_2(s) + Al_2Br_6(g) \rightleftarrows PdAl_2Br_8(g)$ | 8.27 (0.09)[c] | 8.04 (0.14) | 550–750 |
| (B)[b] $PdCl_2(s) + Al_2Cl_6(g) \rightleftarrows PdAl_2Cl_8(g)$ | 6.61 (0.13) | 8.59 (0.20) | 500-800 |

[a] Determined from $RT \ln k_c = T\Delta S - \Delta H$ assuming $\Delta H$ and $\Delta S$ are constant over the entire temperature range. [b] The $\Delta H$ and $\Delta S$ values have been recalculated from the original data of ref 2 using eq 6 and the procedure described in the text. [c] Numbers in parentheses indicate standard deviations as derived from a least-squares treatment of the data.

Emmenegger,[21] can account for a major part of the difference in the enthalpies of reactions A and B.

From the thermodynamic data of Table III, it can be shown that for equal starting pressures ($P_0$ = 1 atm) of $Al_2Cl_6$ and of $Al_2Br_6$, the chloride will volatilize three times more Pd(II) than the bromide in the temperature range from 550 to 750 K. Hence, $Al_2Cl_6$ is a more effective gas-complexing agent than $Al_2Br_6$ for the respective palladium halides in this temperature range. However, one advantage of the bromide over the chloride is that the aluminum bromide will not etch the quartz glass at temperatures up to 800 K, as does the chloride. The thermodynamics of the reaction of $AlBr_3$ with the fused silica does not become favorable until temperatures in excess of 800 K. Even at 1000 K, we found that the $AlBr_3$ did not noticeably react with the glass for several hours.

**Electronic Absorption Spectra.** All known palladium(II) compounds with chloride or bromide ligands possess a square-planar $PdX_4^{2-}$ species as either an isolated ion or a contributing unit into a bridged structure. This coordination has been found to exist in many solid compounds,[22,23] in aqueous solution,[22] and in the gas phase.[24] Recently, Martin and co-workers[22] have established the assignment of the electronic spectral bands of $PdX_4^{2-}$. Polarization and temperature-dependence studies in crystalline $K_2PdX_4$ compounds have shown that (1) the energies of the two d → d transitions, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$, overlap in aqueous solutions to form one broad band near 1.9–2.0 $\mu m^{-1}$, and (2) the molar absorptivity of these overlaping bands increases rapidly with increasing temperature. In Table IV the absorption spectra and assignment of bands for $PdX_4^{2-}$ are compared with the spectra for the two palladium(II) gaseous halide complexes. The energies of the strong d → d band found in aqueous solution are similar to those found in the gaseous complexes. Furthermore, the molar absorptivities near 2.0 $\mu m^{-1}$ of the gaseous complexes listed are also close to the values expected from the temperature dependence of the $K_2PdX_4$ spectra.[22] Thus, the comparison of the visible spectra, in Table IV, tentatively suggests a square-planar coordination for the Pd(II) in these gaseous complexes.

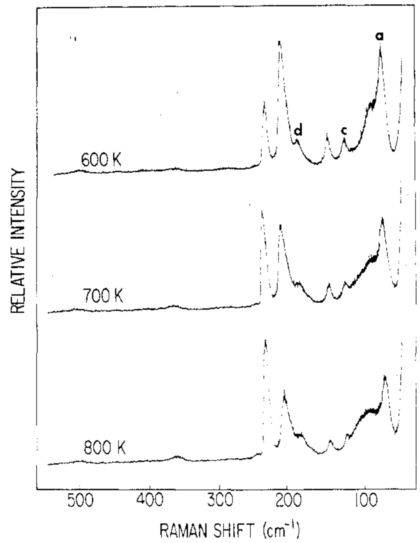

**Figure 4.** Temperature dependence of the Raman spectra of $PdAl_2Br_8$–$Al_2Br_6$–$AlBr_3$ vapors: $P_0 = 2.07 \times 10^{-3}T$ atm; $\lambda_0$ = 488.0 nm; laser power 1 W; spectral slit width ~6 $cm^{-1}$; scan speed 4 nm/min; time constant 0.6 s; polarization $\perp,\perp$.

The UV spectra in aqueous solution or crystalline $K_2PdX_4$[22] are definitely different from those of the vapor complexes. The three charge-transfer bands of $PdBr_4^-$ are replaced in $PdAl_2Br_8$ by one strong band and one shoulder band. The origin of these bands is respectively attributed to the ${}^1A_{1g} \rightarrow {}^3E_u$ and ${}^1A_{1g} \rightarrow {}^1E_u$ ligand-to-metal transitions. The energy shift of the $PdAl_2Br_8$ bands to higher energies, relative to the aqueous solution bands, is probably due, as in the case of $PdAl_2Cl_8$,[1] to the presence of the Al(III) in the second coordination sphere of Pd(II). The high polarizing power of Al(III) hinders the L → M charge-transfer transition and thus shifts the bands to higher energies. A further support of the assignment is the similarity of the intensity of the 3.55-$\mu m^{-1}$ band to that of the 3.02-$\mu m^{-1}$ band in aqueous solution. The ambient temperature molar absorptivity of the complex, extrapolated from the temperature-dependent spectra in Figure 1, is $\epsilon_{35.5}$ ~11 800 L/(mol cm) which is close to the value $\epsilon_{30.2}$ ~10 600 L/(mol cm) found in aqueous solution.

**Raman Spectra.** Figure 4 shows representative Raman spectra of the $PdAl_2Br_8$–$Al_2Br_6$–$AlBr_3$ gas mixture excited with the 488.0-nm laser line. A cell was used that had an aluminum bromide pressure $P_0 = 2.07 \times 10^{-3}T$ atm, a vapor complex pressure $P_c$ ~ 0.06 atm (at 600 K), and no excess of $PdBr_2(s)$ present. The Raman bands due to the vapor complex were deduced by comparison with the spectra of pure aluminum bromide (Figure 5) having $P_0 = 1.97 \times 10^{-3}T$ atm. Thus, the spectra shown in Figure 4 and 5 were obtained from cells having approximately equal aluminum bromide pressures. The two sets of spectra reveal two bands for the $PdAl_2Br_8$ complex

**Table IV.** Absorption Bands and Assignments for Palladium(II) Halides in Vapor Complexes and Solution[a]

| | $PdBr_4^{2-}$, aq soln[b] | | $PdAl_2Br_8$,[c] 500 K | | $PdCl_4^{2-}$, aq soln[b] | | $PdAl_2Cl_8$,[d] 700 K | |
|---|---|---|---|---|---|---|---|---|
| transition | $\nu$ | $\epsilon$ | $\nu$ | $\epsilon$ | $\nu$ | $\epsilon$ | $\nu$ | $\epsilon$ |
| ${}^3A_{2g}$; ${}^3E_g$ | 16.21 | 12 | (14)[e] | (90)[e] | 15.35 | 3 | (15)[e] | |
| | | | | | 17.00 | 7 | | |
| ${}^1A_{2g}$ | 20.05 | 250 | 19.6 | 331 | 20.82 | 100 | 20 | 220 |
| ${}^1E_g$ | | | | | 22.42 | 78 | | |
| ${}^3E_u(L \rightarrow M)$ | 26.99 | 3700 | (27)[e] | (700)[e] | | | | |
| ${}^1E_u(L \rightarrow M)$ | 30.20 | 10600 | | | 35.73 | 9330 | | |
| ${}^1A_{2u}(L \rightarrow M)$ | (30.9)[f] | (>500)[f] | 35.5 | 9740 | | | 40.2 | ~15800 |
| ${}^3E_u(L \rightarrow M)$ | 36.50 | 5400 | | | | | | |
| ${}^1E_u(L \rightarrow M)$ | 40.4 | 28900 | | | 44.98 | 25800 | | |

[a] Values of $\nu$ in $cm^{-1} \times 10^3$; values of $\epsilon$ in L/(mol cm). [b] Reference 22. [c] This work. [d] Reference 2. [e] Found by resolving into Gaussians. [f] Found in crystalline $K_2PdBr_4$, according to ref 22.

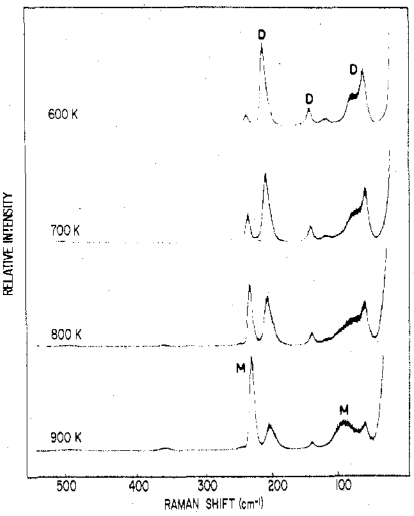

**Figure 5.** Temperature dependence of the Raman spectra of $Al_2Br_6$–$AlBr_3$ vapors: $P_0 = 1.98 \times 10^{-3}$ atm; time constant 0.11 s; remaining spectral conditions as in caption of Figure 4.

at 114 and 180 $cm^{-1}$. The temperature-dependent features of the aluminum bromide spectra (Figure 5) are in accordance with the changes expected in the relative amounts of monomer and dimer from eq 5.[25] Increasing the temperature increases the intensities of the $AlBr_3$ monomer bands (e.g., the $\nu_1$ 230 $cm^{-1}$ and $\nu_4$ 94 $cm^{-1}$ fundamentals) and decreases the intensity of the dimer bands (e.g., the $\nu_2^D$ 203 $cm^{-1}$ and $\nu_4^D$ 59 $cm^{-1}$ fundamentals). Similar effects are observed in Figure 4 where the gaseous mixture containing the $PdAl_2Br_8$ was examined. However, Raman intensity measurements in both sets of spectra relative to the intensity of the 139-$cm^{-1}$ $Al_2Br_6$ band reveal two important differences. First, the dimer peak at 59 $cm^{-1}$ is more intense, relative to all other dimer peaks, in the cells containing the vapor complex than in the cell with pure aluminum bromide. From this observation, we have concluded that another band due to the $PdAl_2Br_8$ complex is superimposed on the 59-$cm^{-1}$ band and contributes to the Raman intensity in this region. Second, for spectra taken at the same furnace temperature, the monomer band intensities are greater in the cell containing the vapor complex than in the cell of pure aluminum bromide, although the $P_0$ pressures in both cells were approximately equal. This effect, as in the case of $PdAl_2Cl_8$ examined previously,[13,26] is probably due to the absorption of the laser line by the d → d band of the $PdAl_2Br_8$, which in turn leads to a higher spectroscopic temperature and an increased dissociation of the $Al_2Br_6$ dimer.

In Table V the Raman frequencies measured for $PdAl_2Br_8$ (bands a, c, and d in Figure 4) are compared with those of $PdAl_2Cl_8$,[13] and the ratio of the chloride and bromide frequencies for the two complexes is calculated. All three bands of the bromide complex were found to be polarized and their frequencies scaled to the corresponding chloride frequencies with a scaling factor between 0.6 and 0.7. Furthermore, spectral measurements using different excitation lines (Figure 1) indicate that the intensities of the three Raman bands increase as the excitation frequency moves away from the maximum of the absorption band. This behavior is analogous to that found for the $PdAl_2Cl_8$ complex and is attributed mainly[27] to resonance Raman interference between weak scattering from d electronic states and strong preresonance scattering from higher energy charge-transfer states.[28,29] This interference leads to a deenhancement of the Raman intensities, as the laser line approaches the d → d band maximum, and has been found to be characteristic of centrosymmetric complexes.[26,30] In other words, it appears that, as in the case of $PdAl_2Cl_8$, the $PdAl_2Br_8$ molecule has a center of symmetry.

**Table V.** Raman Bands Attributed to Gaseous $PdAl_2Br_8$ and $PdAl_2Cl_8$ Molecules

| band | $PdAl_2$-$Br_8$ freq, $cm^{-1}$ | $PdAl_2$-$Cl_8$[a] freq, $cm^{-1}$ | scaling ratio, $\nu_{PdAl_2Br_8}/\nu_{PdAl_2Cl_8}$ | assignment[b] | Raman fundamentals of $PdX_4^{2-}$(aq),[c] $cm^{-1}$ |
|---|---|---|---|---|---|
| I | (59) | 84.5 | 0.65 | $\nu_{ring\ def}$ | $PdBr_4^-$ $\nu_4(B_{2g})$ 97<br>$\nu_2(B_{1g})$ 174<br>$\nu_1(A_{1g})$ 189 |
| II | 114 | 176 | 0.65 | $\delta_{PdX_{2b}}$ | |
| III | 180 | 298 | 0.60 | $\nu_{Pd\text{-}X_t}$ | $PdCl_4^-$ $\nu_4(B_{2g})$ 165<br>$\nu_2(B_{1g})$ 278<br>$\nu_1(A_{1g})$ 304 |

[a] Reference 13 and 26. [b] Based on a $D_{4h}$ configuration of central Pd(II) atom, $D_{2h}$ symmetry for the overall molecule. [c] Reference 29.

The frequency of band III (Table V) is ~23 $cm^{-1}$ below a bridged Al–$Br_b$ frequency and has a value close to the stretching frequency of $PdBr_4^{2-}$ (Table V).[22] This indicates that the Pd(II) in the gaseous complex possesses a square-planar arrangement with the bromides bridged to Al(III). The 9-$cm^{-1}$ difference between the palladium(II)–bromide stretching frequencies, on going from $K_2PdBr_4$ to $PdAl_2Br_8$, is attributed to strong polarization of the bromide by the aluminum counter atom.

In conclusion, the thermodynamic considerations (Table III), the electronic absorption spectra (Table IV), and the Raman spectra suggest that the $PdAl_2Br_8$ gaseous molecule has a structure similar to that of $PdAl_2Cl_8$. A $D_{2h}$ molecular symmetry with Pd(II) as a central ion in a $D_{4h}$ coordination is expected.

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**Registry No.** $PdBr_2$, 13444-94-5; $Al_2Br_6$, 18898-34-5; $PdAl_2Br_8$, 67324-52-1.

**Supplementary Material Available:** Tables I (molar absorptivities) and II (equilibrium experiments) (2 pages). Ordering information is given on any current masthead page.

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# He I Photoelectron Spectra of Gaseous Alkali Nitrates

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The He I photoelectron spectra of the high-temperature gas-phase molecules $KNO_3$, $RbNO_3$, and $CsNO_3$ have been obtained by use of a modified cylindrical-mirror electron spectrometer equipped with an internally located, resistance-heated sample oven. Attempts to obtain data for $LiNO_3$ and $NaNO_3$ were unsuccessful because of decomposition. The identities of the vapor-phase molecules were determined by use of data derived from the techniques of electron diffraction, mass spectrometry, and matrix-isolated infrared spectroscopy. The ionization energies were assigned molecular-orbital origins through the use of MO calculations, comparisons with X-ray and He II photoelectron data from investigations of solids, and analogies with other ionic compounds of similar type.

## 1. Introduction.

In recent years there has been an increasing interest in obtaining UV PES (ultraviolet photoelectron spectroscopy) data on vapors of substances which are solids at room temperature. This interest has stemmed from an attempt to understand better the structure and bonding of high-temperature gas-phase molecules. As yet, very few oxyanion-containing compounds have been investigated, although considerable data have been collected on the gaseous forms of these compounds by mass spectrometry, electron diffraction, and matrix-isolation infrared spectroscopic investigations. In addition, a substantial quantity of X-ray photoelectron data, He II photoelectron data, and X-ray emission data for the solid compounds is available along with numerous theoretical MO calculations for the free anions. The compounds which so far have been studied by UV PES are $TlBO_2$, $TlNO_3$, $Tl_2SO_4$, $TlReO_4$,[1] $LiReO_4$, $NaReO_4$, $KReO_4$, $RbReO_4$, and $CsReO_4$.[2]

The results of several studies of the vapors over heated alkali-metal nitrates indicate different degrees of stability for $LiNO_3$, $NaNO_3$, and $KNO_3$, depending on the pressure, the atmosphere, the composition of the sample container, the rate of heating, and the presence of impurities, especially water. The data from mass spectrometric investigations on $LiNO_3$ and $NaNO_3$ may be taken to indicate considerable decomposition in the 650–750 K range; however, similar studies of $RbNO_3$ and $CsNO_3$ indicate little or no decomposition in the vapor state. These studies and others of related interest which attribute stability to at least some of the alkali-metal nitrates prompted this UV PES investigation of the vapors over heated $LiNO_3$, $NaNO_3$, $KNO_3$, $RbNO_3$, and $CsNO_3$.

## 2. Experimental Procedure

All compounds were commercially obtained, were quoted as being at least 99.9% pure, and, except for drying, were used as obtained.

All spectral measurements presented in this paper were made with a truncated cylindrical-mirror analyzer (as previously described[3]) equipped with a resistance-heated tantalum-strip-wound quartz cell coated with Astroceram, a high-temperature ceramic cement obtained from Chemo-Thermic Industries. The cell was heated by a 0–12 V pulse supply. The procedures for sample heating and spectral accumulation have been described previously[1] and will not be repeated here.

**Table I.** Nitrate Data

| approach | value, eV |
|---|---|
| $KNO_3$ vapor (exptl He I) | 8.96,[a] 9.94,[a] 10.52,[a] 16.13,[a] 16.72[a] |
| $RbNO_3$ vapor (exptl He I) | 8.89,[a] 9.91,[b] 10.59,[b] 15.86,[b] 16.57[b] |
| $CsNO_3$ vapor (exptl He I) | 8.78,[c] 9.84,[b] 10.46,[b] 15.76,[b] 16.63,[d] 17.66,[d] 18.99[d] |
| $NO_3^-$ (ab initio calcn)[e] | $1a_2'$, 9.9; $1e''$, 10.1; $4e'$, 11.4; $3e'$, 17.7; $1a_2''$, 18.9; $4a_1'$, 20.5 |
| $NO_3^-$ (ab initio calcn)[f] | $1a_2'$, 9.9; $1e''$, 10.1; $4e'$, 11.6; $3e'$, 17.8; $1a_2''$, 18.8; $4a_1'$, 20.5 |
| $NO_3^-$ (ab initio calcn)[g] | $1a_2'$, 9.9; $1e''$, 10.0; $4e'$, 11.4; $3e'$, 17.5; $1a_2''$, 19.3; $4a_1'$, 19.6 |
| $NO_3^-$ (ab initio calcn)[h] | $1a_2'$, 9.9; $1e''$, 10.4; $4e'$, 11.9; $3e'$, 17.6; $1a_2''$, 19.1; $4a_1'$, 19.8 |
| $NO_3^-$ (ab initio calcn)[i] | $1a_2'$, 9.9; $1e''$, 9.9; $4e'$, 11.4; $3e'$, 17.5; $1a_2''$, 18.1; $4a_1'$, 20.7 |
| $MNO_3$ solid (exptl X-ray)[j] | $1a_2'$-$1e''$-$4e'$, 10.8; $3e'$-$1a_2''$, 17.2; $4a_1'$, 19.8 |
| $KNO_3$ solid (exptl He II)[k] | $1a_2'$, 9.9; $1e''$, 10.8;[o] $4e'$, 11.6;[o] $3e'$, 16.8; $1a_2''$, 17.4; $4a_1'$, 19.5 |
| $F_3$-CHg-$NO_3$ vapor (exptl He I)[l] | $1a_2'$, 11.1; $1e''$, 12.1; $4e'$, 12.6[n] |
| $TlNO_3$ vapor (exptl He I)[m] | $1a_2'$, 9.9; $1e''$, 11.1; $4e'$, 11.4; $3e'$, 16.7; $1a_2''$, 17.2 |

[a] ±0.03 eV. [b] ±0.04 eV. [c] ±0.06 eV. [d] ±0.07 eV. [e] Reference 18 adjusted by $Q = 4.1$ eV. [f] Reference 20 adjusted by $Q = 4.1$ eV. [g] Reference 19 (without d orbitals) adjusted by $Q = 5.1$ eV. [h] Reference 19 (with d orbitals) adjusted by $Q = 5.5$ eV. [i] Reference 21 adjusted by $Q = 3.6$ eV. [j] Reference 22. [k] Reference 21. [l] Reference 23. [m] Revised interpretation of spectrum in ref 1 with line at 14.2 eV being assigned to a decomposition product. [n] Further lines obscured by $F_3C$ lines. [o] Values obtained by deconvolution.

## 3. Results

Representative spectra of the vapors above heated $KNO_3$, $RbNO_3$, and $CsNO_3$ are presented in Figure 1. Each is typical of 25 or more spectra obtained for each compound. The unlabeled peak in each spectrum is due to methylene

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