Spectroscopic characterization of excited Ca(4s4d3Dj)RG(3Δ1,2) states (RG=Ar, Kr, Xe): No “heavy-atom” mixing of RG(ndδ) character into the wave functions

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The excited Ca(4s4d3Dj)RG(3Δ1,2) states (RG=Ar, Kr, Xe) have been characterized spectroscopically by R2PI (resonance-enhanced two-photon ionization) spectroscopy. The main vibrational progressions, assigned to Ca(4s4d3Dj)RG(3Δ1)←Ca(4s4p3P0)·RG(1Π0−) transitions, have weak subbands 3.7±0.5 cm−1 to the blue which have been assigned to analogous transitions to the 3Δ2 upper states. For CaAr and CaKr, rotational analysis has confirmed this assignment. The 1Δ1/3Δ1 splitting is within experimental error the value expected if the molecular spin-orbit coupling constant is derived entirely from the Ca(4s4d3Dj) atomic contribution. This indicates that there is no “heavy-atom” mixing of RG(ndδ) character into the wave functions of the CaRG(3Δ) states. © 1999 American Institute of Physics. [S0021-9606(99)01526-3]

I. INTRODUCTION

The van der Waals interactions of metal atoms (M) with RG atoms (RG) are one of the simplest examples of solvation at a metal site, and have received wide attention.1 Of particular interest has been1 the variation in bond strengths with (i) the type of outershell M-atom orbital; (ii) the alignment of that orbital with respect to the internuclear axis; and (iii) the polarizability of the RG atom. Spin-orbit (SO) effects in such complexes have also been extensively discussed with regard to mixing of orbital alignment bonding character,1 predissociation,1 and increases in the spin–orbit interaction by addition of “heavy-atom” RG character into nominally metal atom molecular orbitals.1–8

It has been observed in several cases1–8 of low-lying excited “pπ” and “dπ” states of M*·RG (M*=excited metal atom or ion; RG=rare-gas atom) van der Waals complexes that the molecular spin-orbit coupling constant, ASO, is sometimes much larger than that predicted from the atomic spin-orbit coupling constant. ASO is indirectly determined from predissociation. For example, if the molecular spin-orbit coupling constant is derived entirely from the Ca(4s4d3Dj) atomic contribution, this indicates that there is no “heavy-atom” mixing of RG(ndδ) character into the wave functions of the MgAr(3Π) states, and has been confirmed by others.10,11

It is interesting to examine analogous cases of “dδ” outershell M* configurations in M*(ndδ)·RG(Δ) excited states to see if the same kind of direct “heavy-atom” mixing of RG(ndδ) character into the M*·RG(Δ) wave functions can occur. The experimental evidence to date from our laboratories on this question is indirect,5–7 but compelling. The Mg(3s3d3Dj) excited multiplets have a very small atomic spin-orbit coupling constant of ~0.02 cm−1, due to the lack of penetration of the diffuse, excited Mg(3d) orbital to the light Mg nucleus. Consistent with no great increase in the molecular ASO constant on interaction of the Mg(3d) orbital with an Ar atom, the Mg(3s3d3Dj)·Ar(3Δ) ←Mg(3s3p3P0)·Ar(3Π0−) transitions could be adequately rotationally simulated5 assuming Hund’s case “b” character for the 3Δ upper state, e.g., that ASO≈BJ for the upperstate, consistent with ASO being at most a few hundreds of a cm−1. In contrast, the Mg(3s3d3Dj)·RG(3Δ)←Mg(3s3p3P0)·RG(1Π0−) transitions (RG=Kr, Xe) could be reasonably well-simulated5 assuming simple transitions to Hund’s case “a” 3Δ1 upperstate multiplets (P,Q,R structure only). This indicates (indirectly) that the molecular ASO coupling constant has increased from hundreds of wave numbers to several wave numbers. The difference between Kr and Xe vs Ar is reasonable, given that both Kr and Xe atoms have fully occupied valence (3dδ,4dδ, respectively) filled shells of ndδ electrons (albeit inside valence pπ shells, of course), while Ar does not.

Unlike the MgAr(3Δ) case, the analogous Ca(4s4d3Dj)·Ar(3Δ)←Ca(4s4p3P0)·Ar(1Π0−) rotational transitions could be well simulated1 assuming Hund’s case “a” character (3Δ1) in the upperstate. Because Ca(4s4d3Dj) has an atomic spin-orbit coupling constant of ~3.7 cm−1, due to the heavier nature of the Ca atom, however, this case “a” behavior is reasonable, and no mixing of Ar(“3dδ”) character into the wave function was necessary.
to explain the observations.\(^5\) Here we examine new spectra of all the Ca\((4s4d\,\delta\,3\,D_{J})\cdot\text{RG}^{(3\Delta_{1,2})}\)\(-\text{Ca}(4s4p\,\pi\,^{3}P_{J})\cdot\text{RG}^{(3\Pi_{0})}\) transitions (\(\text{RG}=\text{Ar}, \text{Kr}, \text{Xe}\)). In each case, weak "subbands" were observed ~3.7±0.5 cm\(^{-1}\) to the blue of many of the main vibrational transitions to the \(3\Delta_{1}\) upper-state multiplets, and these have been assigned to case "a" (formally forbidden) transitions to the \(3\Delta_{2}\) multiplets which are weakly allowed in an intermediate (case "a")-(case "b") situation such as this one. Successful rotational simulations of both main \(3\Delta_{1}\) and sub-\(3\Delta_{2}\) bands confirm this assignment for the CaAr and CaKr molecules. It is shown that the constant subband splittings, and the \(B\) constant differences for the \(3\Delta_{1}, 3\Delta_{2}\) pairs of bands, are exactly what is expected if the molecular \(A_{SO}\) values are derived solely from the atomic Ca\((4s4d\,\delta\,3\,D_{J})\) SO constant. Thus, no substantial mixing of \(\text{RG}(nd\delta)\) character into the Ca\(^{*}\text{RG}(3\Delta)\) excited state wave functions occurs. This is discussed, and a comparison is made to the analogous Mg\(^{*}\)\-\text{RG}(3\Delta) states.

II. EXPERIMENT

These experiments were carried out using an apparatus constructed for the spectroscopy of, and dynamics within, atom-(RG)\(_{4}\), and atom-(molecule)\(_{n}\) van der Waals complexes using either laser-induced fluorescence (LIF) or resonance two-photon ionization (R2PI) detection. The apparatus is described in more detail elsewhere.\(^5\)-\(^7\)

Briefly, calcium vapor was produced by focusing the second harmonic of a Molectron MY-32/10 Q-switched Nd:YAG laser onto a calcium target rod (1/4 in. diameter machined from Alpha/Aesar 99% pure ingot). An 800 \(\mu\)s pulse of gas produced by a double-solenoid pulsed valve operated at 40 psi backing pressure passed over the calcium rod coincident with the vaporization laser pulse. The gas mixtures utilized were pure Ar, 5% Kr in Ar, and 2.5% Xe in Ar. The Ca vapor/rare gas pulse then passed through a 1.8 mm orifice after having traveled 4 mm from the site of vaporization into the chamber maintained at 6\(\times 10^{-4}\) Torr. The beam, after passing through a 5-mm-diameter skimmer 20 cm from the source, entered the ionization region of a time-of-flight mass spectrometer at a total distance of 60 cm from the source. R2PI spectra are obtained by scanning the output of a dye laser to excite transitions from the Ca\((4s4p\,\pi\,^{3}P_{J})\cdot\text{RG}^{(3\Pi_{0}, \bullet, \nu'' = 0, J''})\) metastable states. Photoionization with a simultaneously pumped ionization dye laser created ions which were detected after a 1-m free-flight region. Dyes used were Coumarin 440 and 480 for resonance, Coumarin 440 for ionization.

III. RESULTS

A. Vibrational progressions

Shown in Figs. 1–3 are the vibrational main progressions, assigned to the Ca\((4s4d\,\delta\,3\,D_{J})\cdot\text{RG}^{(3\Delta_{1})}\)\(-\text{Ca}(4s4p\,\pi\,^{3}P_{J})\cdot\text{RG}^{(3\Pi_{0})}\) transitions, for \(\text{RG}=\text{Ar}, \text{Kr}, \text{Xe}\). The vibrational assignments were based on isotopic splitting measurements. Shown in Fig. 4 are the isotopic band-origin shifts calculated and measured for \(^{40}\text{Ca}\,\alpha\text{Kr}\) for our assignment of \(\nu'\), plus those calculated for an assignment with vibrational quantum numbers greater by one. The assignment is certain, and is consistent with the first strong band in the spectrum in Fig. 2 being the \((0,0)\) band. Shown in Fig. 5 are the measured and calculated isotopic band-origin shifts for \(^{40}\text{Ca}\,\alpha\text{Xe}\) vs \(^{40}\text{Ca}\,\beta\text{Xe}\) for our assignment of \(\nu'\), plus those calculated for an assignment with vibrational quantum numbers greater by one. Again, the assignment is certain, and consistent with the obvious \((0,0)\) band assignment. The analogous CaAr isotopic splitting plot has been published previously.\(^12\) Upon close examination of the spectra, most of the bands in Figs. 1–3 are found to have weak subbands ~3.7±0.5 cm\(^{-1}\) to the blue of the main bands, and we have assigned these subbands to transitions to the \(3\Delta_{2}\) multiplets. In Table I are listed all the band origins of the main bands and the subbands in Figs. 1–3.
B. High-resolution rotational structure of CaAr bands

High-resolution spectra of all the CaAr bands in Fig. 1 have previously been successfully rotationally simulated as Ca(4s4d3/2D1)·Ar[3Δ1]→Ca(4s4p3/2P0)·Ar[3Π0] transitions, e.g., as (Ω′=1)→(Ω″=0) transitions, with simple PQR structure.12 Our contention is that with the moderate $\Delta J/\Delta S$ splitting of only ~3.7 cm$^{-1}$, the $\Delta S$ state is somewhat intermediate between pure Hund’s case ‘‘a’’ and pure Hund’s case ‘‘b,’’ however, so that the ‘‘subband’’ transitions to the $\Delta S$ multiplet are weakly allowed. In pure Hund’s case ‘‘b,’’ the rotational energy level spacings would no longer be determined by $J$ but by the quantum number $N$, and a $\Delta S(b)\leftrightarrow\Delta S(a)$ transition would have complicated structure. But since the $\Delta S$ states are actually closer to case ‘‘a,’’ so that $\Omega$ is still an approximately good quantum number, we have attempted to simulate a new high-resolution $\Delta S\leftrightarrow\Delta S$-subband spectrum using a $(\Omega′=1)\leftrightarrow(\Omega″=0)$ transition, but leaving out all transitions for which $\Delta J$ is not 0 or ±1. The $R(0)$, $P(2)$, and $Q(1)$ branch intensities, included in the ‘‘main-band’’ simulations, were thus set to zero for the subband simulations. [This is equivalent to a $(\Omega′=2)\leftrightarrow(\Omega″=1)$ transition.]

Shown in Fig. 6 is the experimental (5,0) $\Delta S\leftrightarrow\Delta S$ subband, and the successful computer simulation of the rotational structure. The band contours near the origin were less well simulated if the $R(0)$ and $Q(1)$ branches were included rather than left out. This is consistent with, but is not definitive proof of, the band assignment. However, the substantial difference in the observed $B_0′$ rotational constant for the subband versus the main-band is. The best-fit value of $B_0′$ for the simulation in Fig. 6 is 0.0711 cm$^{-1}$, while $B_0′$ for the main band was determined to be 0.0686 cm$^{-1}$ [the known12,13 value of $B_0′=0.0555$ cm$^{-1}$ was used in both simulations, and the uncertainty in the $\Delta B$ values is small]. When $A>B_c$, the dependence on $\Lambda$ and $\Sigma$ of the ‘‘effective’’ $B$ constants of case ‘‘a’’ triplet states is given

\[ B_{0\text{a}}(\Lambda,\Sigma) = \begin{cases} B_{0\text{a}}(0,0) & \text{if } \Lambda = \Sigma = 0, \\ B_{0\text{a}}(0,1) & \text{if } \Lambda = 0, \Sigma = 1, \\ B_{0\text{a}}(1,0) & \text{if } \Lambda = 1, \Sigma = 0, \\ B_{0\text{a}}(1,1) & \text{otherwise}. \end{cases} \]
explained above results in a "best-fit" simulation (see above section on CaAr spectra). A similar analysis to that explained above results in $B'_e(3\Delta_2)=0.0545\text{ cm}^{-1}$, leading to a prediction of $B'_e(3\Delta_1)=0.0526\text{ cm}^{-1}$ compared to the observed value of $B'_e(3\Delta_1)=0.0529\text{ cm}^{-1}$. This shows that our assignment of the upperstate of the subbands to the $3\Delta_2$ multiplet is also correct for the CaKr case.

Sufficient rotational resolution of neither the CaXe main bands, nor a subband, was achieved, so the CaXe assignments in Table I must be formally regarded as tentative at this stage (but probably correct; see Sec. IV).

C. High-resolution rotational structure of the CaKr bands

The rotational structures of several of the main bands were obtained in high resolution and were successfully simulated assuming the same $3\Delta_1\rightarrow\Pi_0^-$ band structure (a small population of the $3\Pi_0^-$ lower state ($10\pm5\%$) is known to be present in the CaKr case, $\sim 1.16\text{ cm}^{-1}$ higher in energy than the $3\Pi_0^-$ state). Shown in Figs. 7–10 are experimental spectra and computer simulations of several bands. We have also been able (with difficulty) to record a subband at sufficient resolution for computer simulation, the (4,0) subband, shown in Fig. 11 along with the "best-fit" simulation (see above section on CaAr spectra). A similar analysis to that explained above results in $B'_e(3\Delta_2)=0.0545\text{ cm}^{-1}$, leading to a prediction of $B'_e(3\Delta_1)=0.0526\text{ cm}^{-1}$ compared to the observed value of $B'_e(3\Delta_1)=0.0529\text{ cm}^{-1}$. This shows that our assignment of the upperstate of the subbands to the $3\Delta_2$ multiplet is also correct for the CaKr case.

D. Spectroscopic constants

From linear Birger–Sponer plots, $\omega_e$ and $\omega_e x_e$ upper-state values were determined, and $D_e\left[=(\omega_e^2/4\omega_e x_e)\right]$ values were estimated. However, more accurate values of $D_0$ (and $D_e$) can be obtained, we believe, from the estimated $D_0$ values for the more weakly bound lower $3\Pi_0^-$ states, and a thermochemical cycle:

$$D_0(3\Delta_1)=D_0(3\Pi_0^-) + E(3\Delta_1) - E(3\Pi_0^-) - \nu_{0,0}.$$ 

Both values are listed in Table II.

FIG. 7. High-resolution spectrum, and computer simulation, of the (0,0) band, CaKr ($3\Delta_1$); simulation parameters: $T=1.0\text{ K}$; laser linewidth: 0.08 cm$^{-1}$; $B''_e=0.0430\text{ cm}^{-1}$; $B''_p=0.0586\text{ cm}^{-1}$; $0^+$/$0^-$ energy separation: $+1.16\text{ cm}^{-1}$; $0^+$/$0^-$ population ratio: 0.08; saturated line strengths.

FIG. 8. High-resolution spectrum, and computer simulation, of the (2,0) band, CaKr ($3\Delta_1$); simulation parameters: same as Fig. 7, except $B''_2=0.0555\text{ cm}^{-1}$.

FIG. 9. High-resolution spectrum, and computer simulation, of the (5,0) band, CaKr ($3\Delta_1$); simulation parameters: same as Fig. 7, except $B''_5=0.0513\text{ cm}^{-1}$.
IV. DISCUSSION

A. No mixing of RG($n\delta\delta$) character into the Ca(4s4d$^3D_J$)·RG($^3\Delta_{12}$) wave functions

The atomic Ca(4s4d$^3D_J$) spin-orbit coupling constant $\xi_{\delta}$ is 3.7 cm$^{-1}$ [$\{E_{1}\bar{D}_{J}^\prime} - E_{1}\bar{D}_{J}\}(2/5)$]. Since $\langle 3\Delta_{1}|H_{\text{SO}}|3\Delta_{1}\rangle$ = $\langle \delta^+ | \beta | a_{\delta} \rangle \langle \delta^+ | \beta \rangle \langle \zeta_{\delta} | | \delta^+ \rangle$, $\xi_{\delta}$ = $\langle \delta^+ | \beta | a_{\delta} \rangle \langle \zeta_{\delta} | | \delta^+ \rangle$ = $\langle \delta^+ | \beta | a_{\delta} \rangle \langle \zeta_{\delta} | | \delta^+ \rangle$ = $\langle \delta^+ | \beta | a_{\delta} \rangle \langle \zeta_{\delta} | | \delta^+ \rangle$, this is equal to $\langle \delta^+ | \beta | a_{\delta} \rangle \langle \zeta_{\delta} | | \delta^+ \rangle$. Thus, $E_{1}\bar{D}_{J}^\prime$ = $E_{1}\bar{D}_{J}$ = $\bar{\zeta}_{\delta}$ for the $^3\Delta_{1}$ state. But since $T_0 = T_0 + A\Lambda \Sigma$, $E_{1}\bar{D}_{J}^\prime$ = $E_{1}\bar{D}_{J}^\prime$ + $A(2)(-1)$, so $E_{1}\bar{D}_{J}^\prime - E_{1}\bar{D}_{J} = 2\bar{\Lambda} \delta = 3.7$ cm$^{-1}$ = $\bar{\xi}_{\delta}$; and $\bar{\zeta}_{\delta}$ = $\bar{\xi}_{\delta}$ = 1.85 cm$^{-1}$. Thus, the observed $^3\Delta_{1}/^1\Delta_{1}$ energy splitting of 3.7±0.5 cm$^{-1}$ is exactly what is expected from the asymptotic Ca(3$D_J$) SO coupling constant, showing that any mixing of RG($n\delta\delta$) character into the Ca(4s4d$^3D_J$)·RG($^3\Delta_{12}$) wave functions is insufficient to change the $\bar{\Lambda}$ value from the expected 1.85 cm$^{-1}$.

B. Comparison with the analogous Mg(3$s3d\delta^3D_J$)·RG states

As discussed in Sec. I, the apparent case “‘a’” nature of the 3$\delta^3\Delta$ states of MgKr and MgXe appears to indicate that there is a mixing of Kr(3$\delta$) and Xe(4d$\delta$) character sufficient to increase the effective SO coupling from ~0.02 cm$^{-1}$ to as much as several cm$^{-1}$. A careful reexamination of the MgRG(3$\Delta$) spectra showed no evidence of subbands, however, so molecular $\Lambda_{\text{SO}}$ coupling constants have not been directly measured for these states.

It is possible that the interaction (and thus mixing) of the Mg(3$s3d\delta^3D$) orbital with the Kr(3$\delta$) and Xe(4d$\delta$) or-

### Table I. Band origins for the $^3\Delta_{12}$$^3\Pi_{0}$ transitions (+ 20 000 cm$^{-1}$) (taken mostly from maxima in low-resolution scans).

<table>
<thead>
<tr>
<th>Transitions</th>
<th>$^4\text{Ca}^{40}\text{Ar}$</th>
<th>$^4\text{Ca}^{40}\text{Kr}$</th>
<th>$^4\text{Ca}^{129}\text{Xe}$</th>
</tr>
</thead>
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<tr>
<td>$^3\Delta_1$</td>
<td>2041.1</td>
<td>2103.9</td>
<td>2171.5</td>
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<td>$^3\Delta_2$</td>
<td>2154.4</td>
<td>2158.4</td>
<td>1792.0</td>
</tr>
<tr>
<td>$^3\Delta_1$</td>
<td>2251.7</td>
<td>2255.7</td>
<td>1922.5</td>
</tr>
<tr>
<td>$^3\Delta_2$</td>
<td>2337.0</td>
<td>2341.0</td>
<td>1922.5</td>
</tr>
<tr>
<td>$^3\Delta_1$</td>
<td>2375.7</td>
<td>2379.7</td>
<td>2096.3</td>
</tr>
<tr>
<td>$^3\Delta_2$</td>
<td>2411.7</td>
<td>2415.7</td>
<td>1742.8</td>
</tr>
<tr>
<td>$E_{3\Delta_1} - E_{3\Delta_2}$ (cm$^{-1}$)</td>
<td>3.9±0.5</td>
<td>3.7±0.5</td>
<td>3.6±0.5</td>
</tr>
</tbody>
</table>
bitals is much stronger than for the Ca(4s4d3D) case, increasing the $A_{SO}$ to $>4$ cm$^{-1}$, and thus perhaps decreasing the subband intensities below detection limits (purer case "a" character). The bond strengths of the CaKr(3$\Delta_1$) and CaXe(3$\Delta_1$) states are much less, and the bond lengths much longer than for the MgKr(3$\Delta_1$) and MgXe(3$\Delta_1$) analog, consistent with this idea.

C. van der Waals bonding in "valence" M(nsnd$\delta^3D$) · RG(3$\Delta$) states

Shown in Table III are $D_e$, $\omega_e$, and $R_e$ values for several states of CaRG neutrals and ions. As can be seen the excited CaRG(3$\Delta$) states are quite strongly bound, approaching even the bond strengths of the Ca$^+$-RG ions. This can be rationalized by the fact that the RG atoms approach along the nodal axis of the excited, diffuse Ca(4d$\delta$) orbital. Thus, repulsion with RG outershell electron density is minimized, and the RG atoms see something approximating the "bare" Ca$^+$ ion core at small $R$. The bond energies are thus only slightly less than the Ca$^+$(4s) · RG ion bond energies. This is in contrast to the lower-state Ca(4s4d3P) · RG(3$\Pi_0$) bond energies, where the Ca(4p) orbital is much lower in energy [15 000 cm$^{-1}$ vs. 38 000 cm$^{-1}$ for the Ca(4d$\delta$) orbital] and is thus less diffuse, leading to more repulsion and lower relative bond energies, even though the RG atom also approaches along the Ca(4p) nodal axis.

Table III. Bond energies, vibrational frequencies, and bond lengths of several CaRG and Ca$^+$RG states.

The percent of the bond energies of the Ca(4d$\delta^3\Delta$) · RG states versus those of the respective Ca$^+$RG ions also increases (73%, 79%, 89%) in the order RG=Ar, Kr, Xe. A similar trend is observed for the first Ca(5s$^3\Sigma^+$) Rydberg states (79%, 80%, 94%), where it is thought that the RG atom can "penetrate" beneath the outer Ca(5s) lobes of electron density and also feel an attraction approaching that of the Ca$^+$RG ions at small $R$.

The fundamental vibrational frequencies $\omega_e$ of the Ca(4d$\delta^3\Delta$) · RG states are also similar to (usually slightly lower than) those of the analogous Ca$^+$ · RG ions. In contrast, the Ca(5s$^3\Sigma^+$) Rydberg states have much higher relative values of $\omega_e$, and this is thought to be due to the fact that at large $R$, as the RG atoms attempt to penetrate the Ca(5s) outerlobe, there is either a maximum or a "flatness" in the potential curve, so that when the "Ca$^+$RG" attraction suddenly sets in at smaller $R$, the potential curves are narrower, leading to higher vibrational frequencies (but similar $D_0$ and $R_0$ values).

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9 R. J. Buenker (private communication).