

# Spectroscopic characterization of excited $\text{Ca}(4s4d\delta^3D_J)\text{RG}(^3\Delta_{1,2})$ states (RG=Ar, Kr, Xe): No “heavy-atom” mixing of $\text{RG}(nd\delta)$ character into the wave functions

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The excited  $\text{Ca}(4s4d\delta^3D_J)\text{RG}[^3\Delta_{1,2}]$  states (RG=Ar, Kr, Xe) have been characterized spectroscopically by R2PI (resonance-enhanced two-photon ionization) spectroscopy. The main vibrational progressions, assigned to  $\text{Ca}(4s4d\delta^3D_1)\text{RG}[^3\Delta_1] \leftarrow \text{Ca}(4s4p\pi^3P_0) \cdot \text{RG}[^3\Pi_0^-]$  transitions, have weak subbands  $3.7 \pm 0.5 \text{ cm}^{-1}$  to the blue which have been assigned to analogous transitions to the  $^3\Delta_2$  upper states. For CaAr and CaKr, rotational analysis has confirmed this assignment. The  $^3\Delta_2/^3\Delta_1$  splitting is within experimental error the value expected if the molecular spin-orbit coupling constant is derived entirely from the  $\text{Ca}(4s4d^3D_J)$  atomic contribution. This indicates that there is no “heavy-atom” mixing of  $\text{RG}(nd\delta)$  character into the wave functions of the  $\text{CaRG}(^3\Delta)$  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.<sup>1</sup> Of particular interest has been<sup>1</sup> 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,<sup>1</sup> predissociation,<sup>1</sup> and increases in the spin-orbit interaction by addition of “heavy-atom” RG character into nominally metal atom molecular orbitals.<sup>1-8</sup>

It has been observed in several cases<sup>1-8</sup> of low-lying excited “ $p\pi$ ” and “ $d\pi$ ” states of  $\text{M}^* \cdot \text{RG}$  ( $\text{M}^*$ =excited metal atom or ion; RG=rare-gas atom) van der Waals complexes that the molecular spin-orbit coupling constant,  $A_{SO}$ , is sometimes much larger than that predicted from the atomic spin-orbit coupling constant of the  $\text{M}^*$  excited multiplet states to which the  $\text{M}^* \cdot \text{RG}$  states correlate at large internuclear distances  $R$ . It now appears, at least for low-lying excited states  $\text{M}^*$ , that such increases in  $A_{SO}$  values usually result from *direct* heavy-atom mixing of  $\text{RG}(np\pi)$  valence character into the  $\text{M}^* \cdot \text{RG}$  wave functions at small internuclear distances  $R$ . This is consistent both with (i) the *regular* (rather than inverted) nature of the  $\Omega$  multiplets, even with large increases in  $A_{SO}$ , and (ii) the increase of  $A_{SO}$  as  $v'$  decreases, consistent with greater mixing of  $\text{RG}(np\pi)$  valence character at smaller “effective” distances  $R$ . The direct mixing was first demonstrated by Buenker<sup>8,9</sup> for the

$\text{LiAr}(^2\Pi)$  states, and has since been confirmed by others.<sup>10,11</sup>

It is interesting to examine analogous cases of “ $d\delta$ ” outershell  $\text{M}^*$  configurations in  $\text{M}^*(nd\delta) \cdot \text{RG}(\Delta)$  excited states to see if the same kind of direct “heavy-atom” mixing of  $\text{RG}(nd\delta)$  character into the  $\text{M}^* \cdot \text{RG}(\Delta)$  wave functions can occur. The experimental evidence to date from our laboratories on this question is indirect,<sup>5-7</sup> but compelling. The  $\text{Mg}(3s3d^3D_J)$  excited multiplets have a very small atomic spin-orbit coupling constant of  $\sim 0.02 \text{ cm}^{-1}$ , due to the lack of penetration of the diffuse, excited  $\text{Mg}(3d)$  orbital to the light Mg nucleus. Consistent with no great increase in the molecular  $A_{SO}$  constant on interaction of the  $\text{Mg}(3d\delta)$  orbital with an Ar atom, the  $\text{Mg}(3s3d\delta^3D_J) \cdot \text{Ar}[^3\Delta] \leftarrow \text{Mg}(3s3p\pi^3P_J) \cdot \text{Ar}[^3\Pi_{0+,0-}]$  transitions could be adequately rotationally simulated<sup>5</sup> assuming Hund’s case “b” character for the  $^3\Delta$  upper state, e.g., that  $A_{SO} < B_J$  for the upperstate, consistent with  $A_{SO}$  being at most a few hundredths of a  $\text{cm}^{-1}$ . In contrast, the  $\text{Mg}(3s3d\delta^3D_J) \cdot \text{RG}(^3\Delta) \leftarrow \text{Mg}(3s3p\pi^3P_J) \cdot \text{RG}(^3\Pi_0)$  transitions (RG=Kr, Xe) could be *reasonably* well-simulated<sup>6,7</sup> assuming simple transitions to Hund’s case “a”  $^3\Delta_1$  upperstate multiplets ( $P, Q, R$  structure only). This indicates (indirectly) that the molecular  $A_{SO}$  coupling constant has increased from hundredths 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* ( $3d\delta, 4d\delta$ , respectively) filled shells of  $nd\delta$  electrons (albeit inside valence  $p\pi$  shells, of course), while Ar does not.

Unlike the  $\text{MgAr}(^3\Delta)$  case, the analogous  $\text{Ca}(4s4d\delta^3D_J) \cdot \text{Ar}(^3\Delta) \leftarrow \text{Ca}(4s4p\pi^3P_0) \cdot \text{Ar}(^3\Pi_0^-)$  rotational transitions could be well simulated<sup>12</sup> assuming Hund’s case “a” character ( $^3\Delta_1$ ) in the upperstate. Because  $\text{Ca}(4s4d^3D_J)$  has an atomic spin-orbit coupling constant of  $3.7 \text{ cm}^{-1}$ , due to the heavier nature of the Ca atom, however, this case “a” behavior is reasonable, and no mixing of  $\text{Ar}(^3d\delta)$  character into the wave function was necessary

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to explain the observations.<sup>12</sup> Here we examine new spectra of all the  $\text{Ca}(4s4d\delta^3D_J) \cdot \text{RG}(^3\Delta_{1,2}) \leftarrow \text{Ca}(4s4p\pi^3P_J) \cdot \text{RG}(^3\Pi_0)$  transitions (RG=Ar, Kr, Xe). In each case, weak "subbands" were observed  $\sim 3.7 \pm 0.5 \text{ cm}^{-1}$  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  $\text{Ca}(4s4d^3D_J)$  SO constant. Thus, no substantial mixing of  $\text{RG}(nd\delta)$  character into the  $\text{Ca}^*\text{RG}(^3\Delta)$  excited state wave functions occurs. This is discussed, and a comparison is made to the analogous  $\text{Mg}^* \cdot \text{RG}(^3\Delta)$  states.

## II. EXPERIMENT

These experiments were carried out using an apparatus constructed for the spectroscopy of, and dynamics within, atom-(RG)<sub>*n*</sub>, and atom-(molecule)<sub>*n*</sub> 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.<sup>5-7</sup>

Briefly, calcium vapor was produced by focusing the second harmonic of a Moletron 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  $\mu\text{s}$  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  $\text{Ca}(4s4p\pi^3P_J) \cdot \text{RG}(^3\Pi_{0-}, v''=0, J'')$  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  $\text{Ca}(4s4d\delta^3D_1) \cdot \text{RG}(^3\Delta_1) \leftarrow \text{Ca}(4s4p\pi^3P_J) \cdot \text{RG}(^3\Pi_{0-})$  transitions, for RG=Ar, Kr, Xe. The vibrational assignments were based on isotopic splitting measurements. Shown in Fig. 4 are the isotopic band-origin shifts calculated and measured for  $^{40}\text{Ca}^{82}\text{Kr}$  vs  $^{40}\text{Ca}^{86}\text{Kr}$  for our assignment of  $v'$ , plus those calculated for an assignment with vibrational quantum numbers greater by

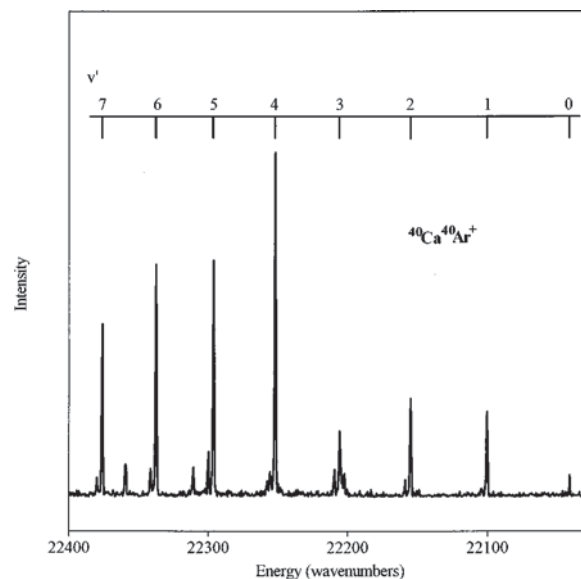


FIG. 1. The  $\text{Ca}(4s4d\delta^3D_1) \cdot \text{Ar}[^3\Delta_1], v' \leftarrow \text{Ca}(4s4p\pi^3P_J) \cdot \text{Ar}[^3\Pi_{0-}], v''=0$  vibrational progression.

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  $^{40}\text{Ca}^{129}\text{Xe}$  vs  $^{40}\text{Ca}^{136}\text{Xe}$  for our assignment of  $v'$ , 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.<sup>12</sup> Upon close examination of the spectra, most of the bands in Figs. 1-3 are found to have weak subbands  $\sim 3.7 \pm 0.5 \text{ cm}^{-1}$  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.

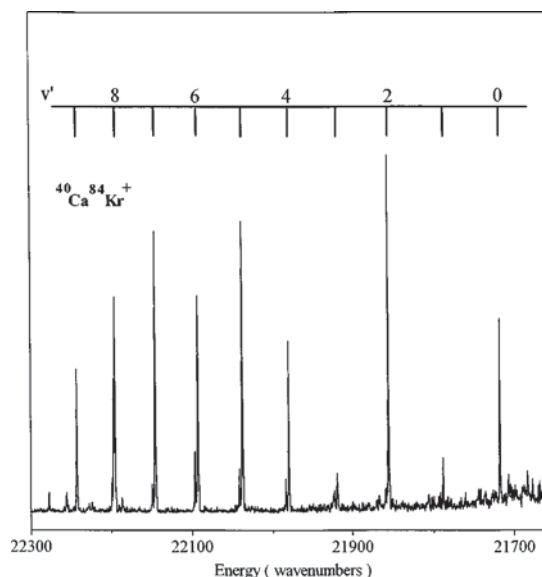


FIG. 2. The  $\text{Ca}(4s4d\delta^3D_1) \cdot \text{Kr}[^3\Delta_1], v' \leftarrow \text{Ca}(4s4p\pi^3P_J) \cdot \text{Kr}[^3\Pi_{0-}], v''=0$  vibrational progression.

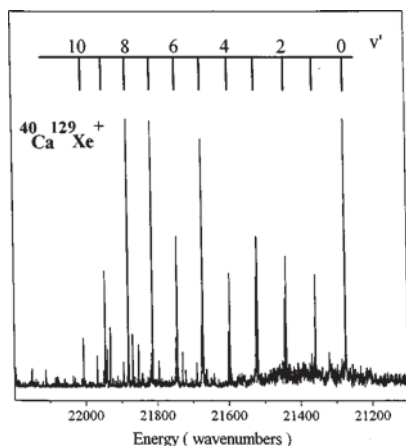


FIG. 3. The  $\text{Ca}(4s4d\delta^3D_1) \cdot \text{Xe}[\ ^3\Delta_1]$ ,  $v' \leftarrow \text{Ca}(4s4p\pi^3P_J) \cdot \text{Xe}[\ ^3\Pi_0^-]$ ,  $v''=0$  vibrational progression.

**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  $\text{Ca}(4s4d\delta^3D_1) \cdot \text{Ar}[\ ^3\Delta_1] \leftarrow \text{Ca}(4s4p\pi^3P_0) \cdot \text{Ar}[\ ^3\Pi_0^-]$  transitions, e.g., as  $(\Omega'=1) \leftarrow (\Omega''=0)$  transitions, with simple  $P, Q, R$  structure.<sup>12</sup> Our contention is that with the moderate  $\ ^3\Delta_1/\ ^3\Delta_2$  splitting of only  $\sim 3.7\text{ cm}^{-1}$ , the  $\ ^3\Delta$  state is somewhat intermediate between pure Hund's case "a" and pure Hund's case "b," however, so that the "subband" transitions to the  $\ ^3\Delta_2$  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  $\ ^3\Delta(b) \leftarrow \ ^3\Pi_0^-(a)$  transition would have complicated  $O, 2P, 3Q, 2R, S$  type branch structure. But since the  $\ ^3\Delta_{1,2}$  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  $\ ^3\Delta_2 \leftarrow \ ^3\Pi_0^-$  subband spectrum assuming a  $(\Omega'=1) \leftarrow (\Omega''=0)$  transition, but leaving out all transitions for which  $\Delta J$  is not 0 or  $\pm 1$ . The  $R(0)$ ,  $P(2)$ , and  $Q(1)$  branch intensities, included in the "main-band"

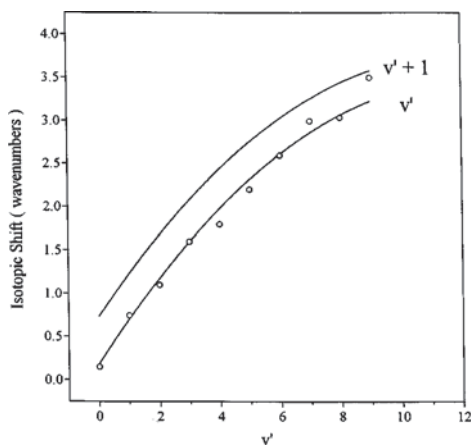


FIG. 4. A plot of the experimental isotopic shifts of the band origins of the  $\ ^{40}\text{Ca}^{82}\text{Kr}$  vs  $\ ^{40}\text{Ca}^{86}\text{Kr}$  isotopomers. Also shown are the theoretically predicted shifts for our assignment as well as an assignment with  $v'+1$ .

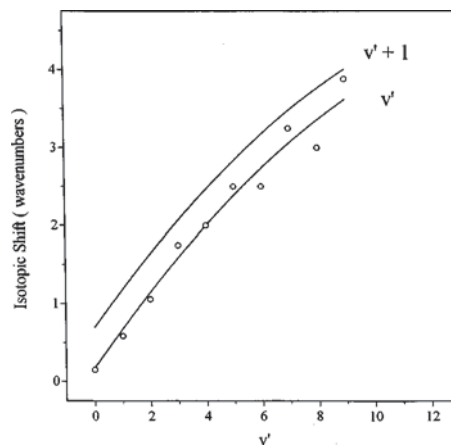


FIG. 5. A plot of the experimental isotopic shifts of the band origins of the  $\ ^{40}\text{Ca}^{129}\text{Xe}$  vs  $\ ^{40}\text{Ca}^{136}\text{Xe}$  isotopomers. Also shown are the theoretically predicted shifts for our assignment as well as an assignment with  $v'+1$ .

simulations, were thus set to zero for the subband simulations. [This is equivalent to a  $(\Omega'=2) \leftarrow (\Omega''=1)$  transition.]

Shown in Fig. 6 is the experimental  $(5,0) \ ^3\Delta_2 \leftarrow \ ^3\Pi_0^-$  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  $B'_2$  rotational constant for the subband versus the main-band is. The best-fit value of  $B'_2$  for the simulation in Fig. 6 is  $0.0711\text{ cm}^{-1}$ , while  $B'_2$  for the main band was determined to be  $0.0686\text{ cm}^{-1}$  (the known<sup>12,13</sup> value of  $B''_0=0.0555\text{ cm}^{-1}$  was used in both simulations, and the uncertainty in the  $\Delta B$  values is small). When  $A \gg B_v$ , the dependence on  $\Lambda$  and  $\Sigma$  of the "effective"  $B$  constants of case "a" triplet states is given

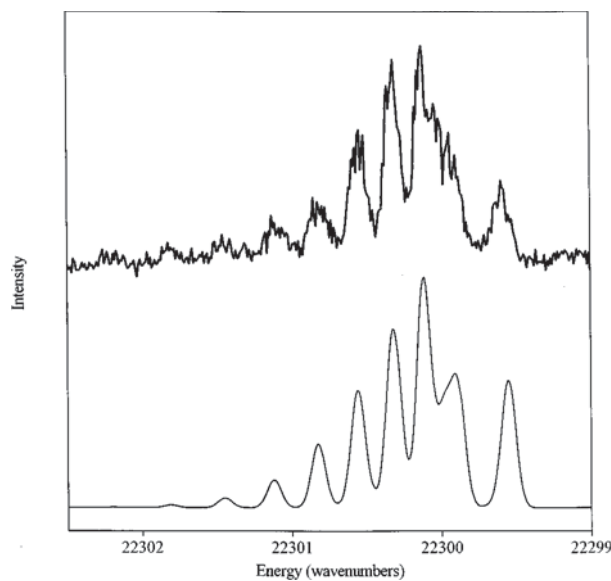


FIG. 6. High-resolution spectrum, and computer simulation, of the  $(5,0)$  subband,  $\text{CaAr}(\ ^3\Delta_2)$ ; simulation parameters:  $T=1.0\text{ K}$ ; laser linewidth:  $0.11\text{ cm}^{-1}$ ;  $B''_0=0.0555\text{ cm}^{-1}$ ;  $B'_2=0.0711\text{ cm}^{-1}$ ; saturated line strengths; intensities of  $R(0)$ ,  $Q(1)$ , and  $P(2)$  transitions were set to zero.

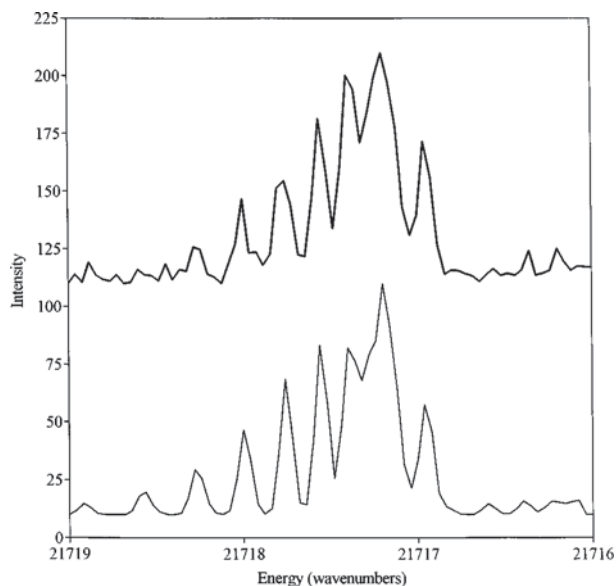


FIG. 7. High-resolution spectrum, and computer simulation, of the (0,0) band, CaKr( $^3\Delta_1$ ); simulation parameters:  $T=1.0$  K; laser linewidth:  $0.08$   $\text{cm}^{-1}$ ;  $B_0''=0.0430$   $\text{cm}^{-1}$ ;  $B_0'=0.0586$   $\text{cm}^{-1}$ ;  $0^+/0^-$  energy separation:  $+1.16$   $\text{cm}^{-1}$ ;  $0^+/0^-$  population ratio:  $0.08$ ; saturated line strengths.

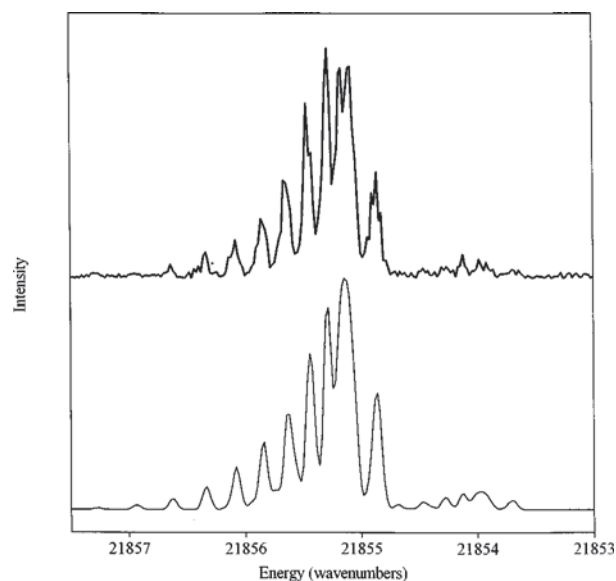


FIG. 8. High-resolution spectrum, and computer simulation, of the (2,0) band, CaKr( $^3\Delta_1$ ); simulation parameters: same as Fig. 7, except  $B_2'=0.0555$   $\text{cm}^{-1}$ .

approximately<sup>14</sup> by:  $B_{\text{eff}}=B_v[1+(2B_v\Sigma/A\Lambda)]$ , where  $A$  is the molecular SO coupling constant, which here is equal to  $\sim 3.7/2=1.85$   $\text{cm}^{-1}$  ( $T_e=T_0+A\Lambda\Sigma$ ; see Sec. IV).<sup>15</sup> For the  $^3\Delta_2$  state, where  $\Sigma=0$ ,  $B'_{\text{eff}(5)}=0.0711$   $\text{cm}^{-1}=B'_5$  (true). For the  $^3\Delta_1$  state, where  $\Sigma=-1$ ,  $B'_{\text{eff}(5)}=0.0711[1-2(0.0711)/(1.85)(2)]=0.0684$   $\text{cm}^{-1}$ , is essentially the same as the  $0.0686$   $\text{cm}^{-1}$  value determined experimentally, within experimental error. This shows that our assignment of the subbands to  $^3\Delta_2$  multiplets is correct for the CaAr case.

### 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  $^3\Delta_1\leftarrow^3\Pi_0^-$  band structure (a small population of the  $^3\Pi_0^+$  lower state ( $10\pm 5\%$ ) is known to be present in the CaKr case,  $\sim 1.16$   $\text{cm}^{-1}$  higher in energy than the  $^3\Pi_0^-$  state).<sup>13</sup> 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  $B'_4(^3\Delta_2)=0.0545$   $\text{cm}^{-1}$ , leading to a prediction of  $B'_4(^3\Delta_1)=0.0526$   $\text{cm}^{-1}$  compared to the observed value of  $B'_4(^3\Delta_1)=0.0529$   $\text{cm}^{-1}$ . 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).

### D. Spectroscopic constants

From linear Birger–Sponer plots,  $\omega_e$  and  $\omega_e x_e$  upper-state values were determined, and  $D_e[(\omega_e^2/4\omega_e x_e)]$  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:

$$D_0(^3\Delta_1)=D_0(^3\Pi_0^-)+E(^3D_1)-E(^3P_0)-\nu_{0,0}.$$

Both values are listed in Table II.

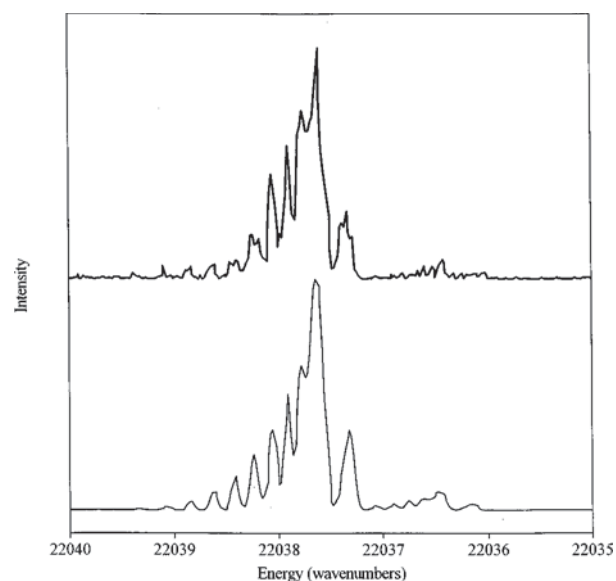


FIG. 9. High-resolution spectrum, and computer simulation, of the (5,0) band, CaKr( $^3\Delta_1$ ); simulation parameters: same as Fig. 7, except  $B'_5=0.0513$   $\text{cm}^{-1}$ .

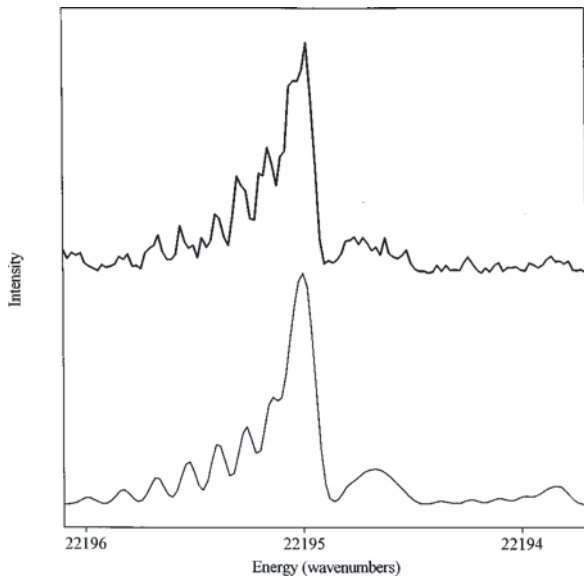


FIG. 10. High-resolution spectrum, and computer simulation, of the (8,0) band, CaKr( $^3\Delta_1$ ); simulation parameters: same as Fig. 7, except  $B'_8 = 0.0479 \text{ cm}^{-1}$ .

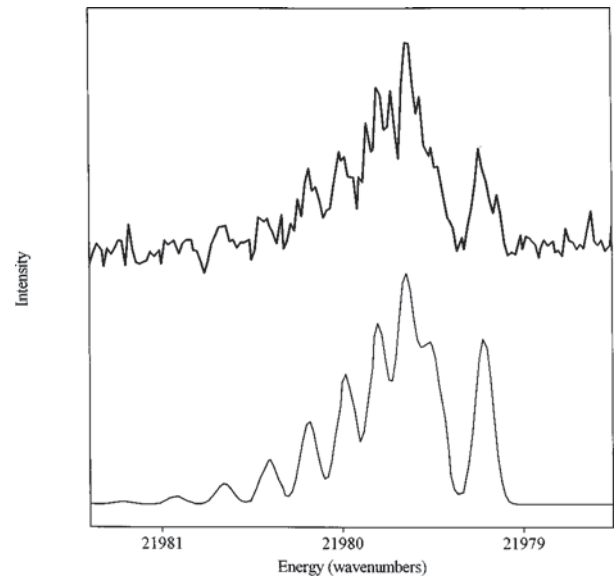


FIG. 11. High-resolution spectrum, and computer simulation, of the (4,0) subband, CaKr( $^3\Delta_2$ ); simulation parameters:  $T=0.8 \text{ K}$ ; laser linewidth= $0.11 \text{ cm}^{-1}$ ;  $B''_0=0.0430 \text{ cm}^{-1}$ ;  $B'_4=0.0545 \text{ cm}^{-1}$ ; saturated line strengths; intensities of  $R(0)$ ,  $Q(1)$ , and  $P(2)$  transitions were set to zero.

From the variation of  $B_{v'}$  with  $v'$ , the  $B'_e$  and  $\alpha'_e$  values were determined, from which  $R'_e$  and  $R'_0$  bond lengths were computed for CaAr and CaKr. This information is listed in Table II.

IV. DISCUSSION

A. No mixing of RG( $nd\delta$ ) character into the Ca( $4s4d\delta^3D_J$ )·RG( $^3\Delta_{1,2}$ ) wave functions

The atomic Ca( $4s4d^3D_J$ ) spin-orbit coupling constant  $\zeta_\delta$  is  $3.7 \text{ cm}^{-1} [(E_{3D_3} - E_{3D_1})(2/5)]$ .<sup>16</sup> Since<sup>16</sup>  $\langle ^3\Delta_1 | H_{SO} | ^3\Delta_1 \rangle = \langle \delta^+ \beta | a_\delta \cdot \hat{\zeta}_z \cdot \hat{s}_z | \delta^+ \beta \rangle$ , and  $\hat{\zeta}_z | \delta^+ \rangle = +2\hbar | \delta^+ \rangle$  and  $\hat{s}_z | \beta \rangle = -\hbar/2 | \beta \rangle$ , this is equal to  $\langle \delta^+ \beta | a_\delta (2\hbar) (-\hbar/2) | \delta^+ \beta \rangle$ . Thus,  $E_{3\Delta_1} = -a_\delta (\hbar)^2 = -\zeta_\delta$  for the  $^3\Delta_1$  state. But since<sup>15</sup>  $T_e = T_0 + A\Lambda\Sigma$ ,  $E_{3\Delta_1} = E_{3\Delta_2} + A(2)(-1)$ , so  $E_{3\Delta_2} - E_{3\Delta_1} = 2A_\delta = 3.7 \text{ cm}^{-1} = \zeta_\delta$ ; and  $A_\delta = \zeta_\delta/2 = 1.85 \text{ cm}^{-1}$ . Thus, the observed  $^3\Delta_2/^3\Delta_1$  energy splitting of  $3.7 \pm 0.5 \text{ cm}^{-1}$  is exactly what is expected from

the asymptotic Ca( $^3D_J$ ) SO coupling constant, showing that any mixing of RG( $nd\delta$ ) character into the Ca( $4s4d\delta^3D_J$ )·RG( $^3\Delta_{1,2}$ ) wave functions is insufficient to change the  $A_\delta$  value from the expected  $1.85 \text{ cm}^{-1}$ .

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

As discussed in Sec. I, the apparent case ‘‘a’’ nature<sup>6,7</sup> of the  $3d\delta^3\Delta$  states of MgKr and MgXe appears to indicate that there is a mixing of Kr( $3d\delta$ ) and Xe( $4d\delta$ ) character sufficient to increase the effective SO coupling from  $\sim 0.02 \text{ cm}^{-1}$  to as much as several  $\text{cm}^{-1}$ . A careful reexamination of the MgRG( $^3\Delta$ ) spectra showed no evidence of subbands, however, so molecular  $A_{SO}$  coupling constants have not been directly measured for these states.

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

TABLE I. Band origins for the  $^3\Delta_{1,2} \leftarrow ^3\Pi_0^-$  transitions ( $+20\,000 \text{ cm}^{-1}$ ) (taken mostly from maxima in low-resolution scans).

	$^{40}\text{Ca}^{40}\text{Ar}$		$^{40}\text{Ca}^{84}\text{Kr}$		$^{40}\text{Ca}^{129}\text{Xe}$	
	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_1$	$^3\Delta_2$	$^3\Delta_1$	$^3\Delta_2$
(0,0)	2041.1	...	1717.5	...	1274.0	...
(1,0)	2099.9	2103.9	1788.0	1792.0	1358.1	...
(2,0)	2154.4	2158.4	1855.0	1858.8	1400.1	1404.1
(3,0)	2205.6	2209.1	1919.5	1922.5	1519.8	1523.8
(4,0)	2251.7	2255.7	1975.8	1979.5	1596.8	1600.3
(5,0)	2295.9	2299.4	2037.50	2041.5	1671.3	1674.3
(6,0)	2337.0	2341.0	2092.5	2096.3	1742.8	1746.3
(7,0)	2375.7	2379.7	2145.0	2148.8	1812.8	1815.8
(8,0)	2411.7	2415.7	2195.0	...	1879.8	...
(9,0)	...	...	2242.5	...	1945.2	...
$E_{3\Delta_2} - E_{3\Delta_1} (\text{cm}^{-1})$	3.9±0.5		3.7±0.5		3.6±0.5	

TABLE II. Spectroscopic constants for the  $\text{Ca}(4s4p\pi^3P_J) \cdot \text{RG}[^3\Pi_0^-]$  and  $\text{Ca}(4s4d\delta^3D_J) \cdot \text{RG}(^3\Delta_1)$  states.

	$^{40}\text{Ca}^{40}\text{Ar}$		$^{40}\text{Ca}^{84}\text{Kr}$		$^{40}\text{Ca}^{129}\text{Xe}$	
	$^3\Pi_0^-$	$^3\Delta_1^a$	$^3\Pi_0^-$	$^3\Delta_1$	$^3\Pi_0^-$	$^3\Delta_1$
$\nu_{0,0}$	...	22041.1	...	21717.5	...	21274.0
$\omega_e$	...	$60.5 \pm 1.0$	...	$72.58 \pm 0.29$	...	$86.42 \pm 0.11$
$\omega_e x_e$	...	$1.61 \pm 0.11$	...	$1.439 \pm 0.028$	...	$1.195 \pm 0.011$
$B_o$	$0.0555 \pm 0.0030^{a,b}$	$0.0811 \pm 0.0030$	$0.0430 \pm 0.0023^b$	$0.05860 \pm 0.0023$	$0.0300 \pm 0.0022^b$	...
$B_e$	...	$0.0822 \pm 0.0030^d$	...	$0.05901 \pm 0.0023^c$	...	...
$\alpha_e$	...	$0.0025 \pm 0.0001$	...	$0.00134 \pm 0.000062$	...	...
$R_o$	$3.90 \pm 0.10^{a,b}$	$3.23 \pm 0.06$	$3.81 \pm 0.10^b$	$3.26 \pm 0.06$	$4.28 \pm 0.15^b$	...
$R_e$	...	$3.20 \pm 0.06^d$	...	$3.25 \pm 0.06^c$	...	...
$D_o$	$60 \pm 50^c$	$609 \pm 50$	$120 \pm 60^c$	$993 \pm 60$	$300 \pm 80^c$	$1616 \pm 80$
		(538)		(879)		(1520)
$D_e$		$639 \pm 50$	...	$1029 \pm 60$		$1659 \pm 80$
		(568)		(915)		(1562)

<sup>a</sup>Reference 12.<sup>b</sup>Reference 13.<sup>c</sup>Reference 17.<sup>d</sup>“True”  $B_e$ , of the  $^3\Delta_2$  state, is  $0.0859 \text{ cm}^{-1}$ ,  $R_e = 3.13 \text{ \AA}$ .<sup>e</sup>“True”  $B_e$ , of the  $^3\Delta_2$  state, is  $0.0609 \text{ cm}^{-1}$ ,  $R_e = 3.20 \text{ \AA}$ .

bitals is much stronger than for the  $\text{Ca}(4s4d\delta^3D)$  case, increasing the  $A_{SO}$  to  $>4 \text{ cm}^{-1}$ , and thus perhaps *decreasing* the subband intensities below detection limits (purer case “a” character). The bond strengths of the  $\text{CaKr}(^3\Delta_1)$  and  $\text{CaXe}(^3\Delta_1)$  states (see Table III) are much less,<sup>5-7,12</sup> and the bond lengths much longer,<sup>5-7,12</sup> than for the  $\text{MgKr}(3d\delta^3\Delta)$  and  $\text{MgXe}(3d\delta^3\Delta)$  analog, consistent with this idea.

### C. van der Waals bonding in “valence” $M(\text{nsnd}\delta^3D_J) \cdot \text{RG}(^3\Delta)$ states

Shown in Table III are  $D_e$ ,  $\omega_e$ , and  $R_e$  values for several states of  $\text{CaRG}$  neutrals and ions. As can be seen the excited  $\text{CaRG}(^3\Delta)$  states are quite strongly bound, approaching even the bond strengths of the  $\text{Ca}^+ \cdot \text{RG}$  ions. This can be rationalized by the fact that the RG atoms approach along the nodal axis of the excited, diffuse  $\text{Ca}(4d\delta)$  orbital. Thus, repulsion with RG outershell electron density is minimized, and the RG atoms see something approximating the “bare”

TABLE III. Bond energies, vibrational frequencies, and bond lengths of several  $\text{CaRG}$  and  $\text{Ca}^+\text{RG}$  states.

	$D_o$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$R_o$ ( $\text{\AA}$ )
$\text{CaAr}(4s4p\pi^3\Pi_0^-)^{a,b,c}$	$60 \pm 50$	...	$3.9 \pm 0.1$
$\text{CaAr}(4s5s^3\Sigma^+)^b$	$564 \pm 50$	81	$3.13 \pm 0.06$
$\text{CaAr}(4s4d\delta^3\Delta_1)^a$	$609 \pm 50$	61	$3.23 \pm 0.06$
$\text{Ca}^+\text{Ar}(4s^2\Sigma^+)$	$775 \pm 50^c$	$69^d$	...
$\text{CaKr}(4s4p\pi^3\Pi_0^-)^{b,c}$	$120 \pm 60$	...	$3.8 \pm 0.1$
$\text{CaKr}(4s5s^3\Sigma^+)^b$	$980 \pm 60$	87	$3.37 \pm 0.08$
$\text{CaKr}(4s4d\delta^3\Delta_1)^e$	$993 \pm 60$	73	$3.26 \pm 0.06$
$\text{Ca}^+\text{Kr}(4s^2\Sigma^+)$	$1244 \pm 60^c$	$77^d$	...
$\text{CaXe}(4s4p\pi^3\Pi_0^-)^{b,c}$	$300 \pm 80$	...	$4.3 \pm 0.2$
$\text{CaXe}(4s5s^3\Sigma^+)^b$	$1705 \pm 80$	106	$3.59 \pm 0.12$
$\text{CaXe}(4s4d\delta^3\Delta_1)^e$	$1616 \pm 80$	86	...
$\text{Ca}^+\text{Xe}(4s^2\Sigma^+)$	$1811 \pm 80^c$	$86^d$	...

<sup>a</sup>Reference 12.<sup>b</sup>Reference 13.<sup>c</sup>Reference 17.<sup>d</sup>Reference 3.<sup>e</sup>This work.

$\text{Ca}^+(4s)$  ion core at small  $R$ . The bond energies are thus only slightly less than the  $\text{Ca}^+(4s) \cdot \text{RG}$  ion bond energies. This is in contrast to the lower-state  $\text{Ca}(4s4p\pi^3P_J) \cdot \text{RG}(^3\Pi_0)$  bond energies, where the  $\text{Ca}(4p\pi)$  orbital is much lower in energy [ $\sim 15\,000 \text{ cm}^{-1}$  vs  $\sim 38\,000 \text{ cm}^{-1}$  for the  $\text{Ca}(4d\delta)$  orbital] and is thus less diffuse, leading to more repulsion and lower relative bond energies, even though the RG atom also approaches along the  $\text{Ca}(4p\pi)$  nodal axis. (The  $^3\Pi_0^-D_0$  values are also substantially further reduced due to the large ( $A_{SO} = 211 \text{ cm}^{-1}$ ) spin-orbit-induced  $\sigma/\pi$  “mixed” character of the  $\Omega = 0^-$  multiplet.)

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

The fundamental vibrational frequencies  $\omega_e$  of the  $\text{Ca}(4d\delta^3\Delta) \cdot \text{RG}$  states are also similar to (usually slightly lower than) those of the analogous  $\text{Ca}^+ \cdot \text{RG}$  ions. In contrast, the  $\text{Ca}(5s^3\Sigma^+)$  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  $\text{Ca}(5s)$  outerlobe, there is either a maximum or a “flatness” in the potential curve, so that when the “ $\text{Ca}^+\text{RG}$ ” 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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- <sup>1</sup>W. H. Breckenridge, C. Jovet, and B. Soep, in *Advances in Metal and Semiconductor Clusters*, edited by M. Duncan (JAI, Greenwich, 1995), Vol. 3.
- <sup>2</sup>J. S. Pilgrim, C. S. Yeh, K. R. Berry, and M. A. Duncan, *J. Chem. Phys.* **100**, 7945 (1994).
- <sup>3</sup>S. H. Pullins, C. T. Scurlock, J. E. Reddic, and M. A. Duncan, *J. Chem. Phys.* **104**, 7518 (1996).
- <sup>4</sup>J. E. Reddic and M. A. Duncan, *J. Chem. Phys.* (in press).
- <sup>5</sup>S. Massick and W. H. Breckenridge, *J. Chem. Phys.* **105**, 9719 (1996).
- <sup>6</sup>J. G. Kaup and W. H. Breckenridge, *J. Chem. Phys.* **107**, 6005 (1997).
- <sup>7</sup>J. G. Kaup and W. H. Breckenridge, *J. Chem. Phys.* **107**, 6014 (1997).
- <sup>8</sup>J.-P. Gu, G. Hirsch, R. J. Buenker, I. D. Petsalakis, G. Theodorakopoulos, and M. B. Huang, *Chem. Phys. Lett.* **230**, 473 (1994).
- <sup>9</sup>R. J. Buenker (private communication).
- <sup>10</sup>S. Matsila and R. M. Pitzer, *J. Phys. Chem. A* **102**, 1652 (1998).
- <sup>11</sup>K. Sohlberg and D. R. Yarkony, *J. Chem. Phys.* **107**, 7690 (1997).
- <sup>12</sup>J. G. Kaup and W. H. Breckenridge, *J. Chem. Phys.* **107**, 5676 (1997).
- <sup>13</sup>J. G. Kaup and W. H. Breckenridge, *J. Chem. Phys.* **107**, 5283 (1997).
- <sup>14</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), p. 235.
- <sup>15</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950), p. 215.
- <sup>16</sup>H. LeFebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).
- <sup>17</sup>J. G. Kaup and W. H. Breckenridge, *J. Chem. Phys.* **107**, 4451 (1997).