JOURNAL OF CHEMICAL PHYSICS VOLUME 109, NUMBER 18 8 NOVEMBER 1998

Spectroscopic characterization of the unusually strongly bound, doubly excited van der Waals state, Mg$(3p\pi 3p\pi\ ^3P_J)\cdot$Kr$[^3\Sigma^-]$

Allen W. K. Leung, John G. McCaffrey,[a] and W. H. Breckenridge
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

(Received 23 June 1998; accepted 3 August 1998)

The unusual doubly excited van der Waal's state, Mg$(3p\pi 3p\pi\ ^3P_J)\cdot$Kr$[^3\Sigma^-]$, has been characterized using a laser-vaporization, supersonic-jet source and R2PI (Resonance Two-Photon Ionization) spectroscopy. This state is very strongly bound ($D_e = 3966\ \text{cm}^{-1}$) and has a short bond length ($R_e = 2.45$ Å) compared to its singly excited analogue, Mg$(3s3p\pi\ ^3P_J)\cdot$Kr$[^3\Pi_{0^-}]$, for which $D_e = 267\ \text{cm}^{-1}$ and $R_e = 3.48$ Å. In fact, this state is even more than twice as strongly bound as the ground-state Mg$(3s)^+\cdot$Kr ion, where $D_e = 1949\ \text{cm}^{-1}$ and $R_e \approx 2.8$ Å. Possible reasons for the strong van der Waal's bonding are discussed, and it is concluded that the lack of σ-σ repulsion because there is no Mg$(3s\sigma)$ valence electron must be a major factor; the similar ionic van der Waal's state Mg$^+(3p\pi)\cdot$Kr$[^2\Pi]$, which would be obtained by removing one of the Mg$(3p\pi)$ electrons, is even more strongly bound, with $D_e \approx 7200\ \text{cm}^{-1}$ [J. S. Pilgrim, C. S. Yeh, K. R. Berry, and M. A. Duncan, J. Chem. Phys. **100**, 7945 (1994)]. *© 1998 American Institute of Physics.* [S0021-9606(98)00642-4]

INTRODUCTION

We have recently discovered[1–3] a new class of neutral doubly excited valence states M*·RG (M*=electronically excited metal atom, RG=rare-gas atom) of van der Waals diatomic molecules which are extremely strongly bound and have very short bond lengths compared to their singly excited valence analogues. For example, the Mg$(3p\pi 3p\pi\ ^3P_J)\cdot$Ar$[^3\Sigma^-]$ state[1] has a very large bond energy of $D_0 = 2850\ \text{cm}^{-1}$ and a short bond length of $R_0 = 2.41$ Å, in contrast to the analogous singly excited Mg$(3s3p\pi\ ^3P_J)\cdot$Ar$[^3\Pi_{0^-}]$ state, for which $D_0 = 160\ \text{cm}^{-1}$,[4] and $R_0 = 3.66$ Å.[5] Even more surprising, the Mg$(3p\pi 3p\pi\ ^3P_J)\cdot$Ar$[^3\Sigma^-]$ state is more than twice as strongly bound as the ground-state MgAr$^+$ ion ($D_0 = 1240\ \text{cm}^{-1}$;[4,6] $R_0 = 2.83$ Å[6]), despite the fact that M$^+$·RG ions have strong ion/induced-dipole attractive forces. The D_0 values for such M$^+$·RG complexes were, in fact, assumed by many of us earlier[7,8] to be upper limits for neutral, excited-state M*·RG D_0 values. The D_0 values for higher energy M*(Rydberg)·RG states, for example, must approach the D_0 values of the M$^+$·RG ions as the principle quantum number ''n'' goes to infinity.[7–10]

We have been attempting to characterize these unusual states experimentally in a more comprehensive manner by varying the identity of M(Mg,Ca,Sr,Ba) and of RG(Ne,Ar,Kr,Xe). These efforts have been frustratingly difficult, however, due (ironically) to the strongly bound and high-energy nature of the doubly excited states. The M(np,np) doubly excited atomic states are, in fact, at energies ⩾80% of the way to the M$(ns)^+$ ionization limit. Thus although they are truly ''valence'' states, they are imbedded in a plethora of states resulting from bonding of highly excited M* Rydberg states with ground-state RG atoms.

Further, the strongly repulsive inner walls of M*·RG potential curves from $nsnp$ or $nsnd$ valence singlet or triplet atomic M* state asymptotes at lower energies can intersect the potential curves of the unusual M$(np\pi np\pi\ ^3P_J)$ ·RG$[^3\Sigma^-]$ states, since the $^3\Sigma^-$ bond strengths are large and their bond lengths are small. This maximizes the possibilities for predissociation to lower energy M*+RG asymptotic products. Using R2PI spectroscopy there is, in principle, no difficulty in characterizing such a transition to a predissociated state, at least if the M* predissociation product can be detected sensitively, since the molecular M·RG transition which is excited simply appears as M$^+$ signal rather than M·RG$^+$ signal in the time-of-flight mass spectrometer, after ionization by a second photon. However, there are two possible difficulties with regard to spectral characterization of these transitions, one inherent to all electronic transitions to predissociated excited states, the other more specific to transitions to these unusually strongly bound doubly excited M*·RG states:

(i) If the total rate of predissociation to lower M*+RG asymptotes is sufficiently high, all rotational structure in the bands (and possibly even the vibrational structure) will be severely broadened, precluding accurate determinations of upper-state R_e values. In the transitions to the Ca$(4p\pi 4p\pi\ ^3P_J)\cdot$Ar$[^3\Sigma^-]$ state, for example, all rotational structure was completely broadened out[2] (the signal-to-noise of the spectra was quite high, but the vibrational peaks were essentially smooth, broad, and Lorentzian in shape even at high resolution).

(ii) If the primary products of the predissociation are the M$(nsnp\ ^3P_J)$ states [or the M$(nsns\ ^1S_0)$ ground states], then it will be impossible to detect the small M(^3P_J), or M$(^1S_0)$, predissociation product concentrations in the huge

---

[a] Visiting Associate Professor, 1998; permanent address: Department of Chemistry, National University of Ireland, Maynooth, County Kildare, Ireland.

''background'' of metastable M(^3P_J), or M($^1S_0$), states from the laser-vaporization sources used to synthesize the M($nsnp$ ^3P_J)$\cdot$RG[$^3\Pi_0$] lower states.

After several attempts, we have finally managed to identify and record an R2PI spectrum of the Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-$]$\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0$] transition with sufficient signal-to-noise for vibrational analysis, and have been able to estimate R_e and D_e values for the $3p\pi3p\pi$ $^3\Sigma^-$ state with reasonable accuracy, using the known (and accurately estimated) spectroscopic constants for the Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0$] lower state, and Franck–Condon simulations. Attempts to obtain the analogous Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Xe[$^3\Sigma^-$]$\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Xe[$^3\Pi_0$] spectrum have so far failed. We believe the low signal-to-noise in the spectra, compared to the analogous MgAr spectra reported earlier, is due to the fact that the MgKr and MgXe $^3\Sigma^-$ states predissociate predominately to the Mg($3p3p$ ^3P_J) states [i.e., problem (ii)], as explained above.

EXPERIMENT

The experiments were carried out in an apparatus designed for spectroscopic and dynamical measurements of atom-(RG)$_n$ and atom-(molecule)$_n$ van der Waals complexes using either LIF (laser-induced fluorescence) or R2PI (resonance two-photon ionization) detection. Only R2PI spectra obtained by TOF (time-of-flight) mass spectrometry were collected in this experiment. The apparatus has been previously described in detail.[1] Briefly, magnesium vapor was produced by focusing the second-harmonic of a Molectron MY-32/10 Q-switched Nd:YAG laser onto a magnesium target rod (1/4 in. Johnson Mathey, 99.8% pure). An 800 μs pulse of gas (~4% Kr in Ar) produced by a double-solenoid pulsed valve operated at 40 psi backing pressure passed over the magnesium rod coincident with the vaporization laser pulse. The Mg vapor/Ar pulse then passed through a 1.8 mm orifice after having traveled 4 mm from the site of vaporization into a chamber maintained at 6×10^{-1} Torr. The beam, after passing through a 5 mm diameter skimmer 20 cm from the source, reaches the ionization region of a TOF mass spectrometer, in a second chamber, at a total distance of 60 cm from the source. The doubled output (KDP, angled tuned) of a Lumonics Hyperdye-300 series dye laser is scanned to excite the Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-,v'$]$\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0,v''=0$] transitions. Subsequent photoionization with a second photon from the fundamental or frequency-doubled laser radiation, or a second Lumonics Hyperdye-300 series laser at ~4878 Å, created ions which were detected after traversing a 1-m free-flight region. Flurol 7GA (Lambda Physik) and Rhodamine 590 (Exciton) laser dyes were used to generate frequency-doubled laser radiation. The ionization photon from the second dye laser, when utilized, was generated using Coumarin 480 (Exciton) laser dye.

RESULTS

As shown in the lower part of Fig. 1, with a 4% Kr/Ar gas mixture at a backing pressure of about 40 psi, when the frequency-doubled dye laser radiation is tuned through the 34 000–36 000 cm^{-1} region to the red of the strong Mg($3p3p$ ^3P_J)$\leftarrow$Mg($3s3p$ ^3P_J) atomic transitions near 36 000 cm^{-1}, a long series of vibrational transitions with high frequencies in the upper-state are observed with low signal-to-noise in the Mg$^+$ mass channels. These bands have been assigned as transitions from Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0$], $v''=0$ to Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-$], $v'=9-22$. Evidence for this assignment is presented below.

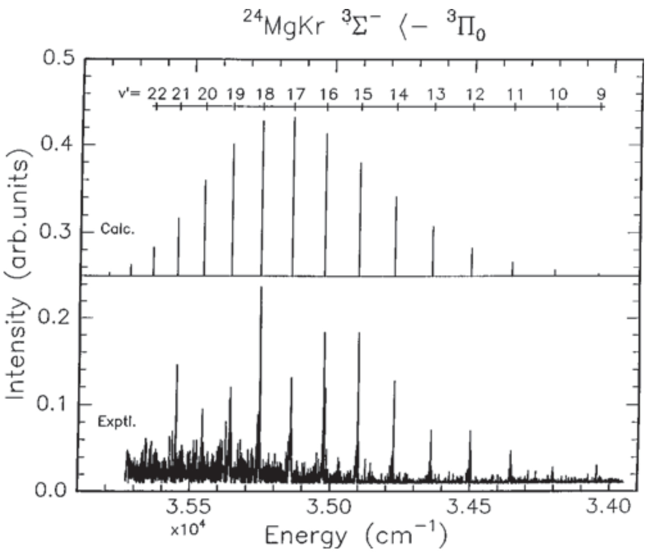

FIG. 1. Shown in the lower part of the figure are peaks in the ^{24}Mg$^+$ mass channel which have been assigned as Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-$], (v') $\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_{0\pm}$], ($v''=0$) transitions. Three strong Mg atomic lines at 35 051 cm^{-1}, 35 098 cm^{-1}, and 35 118 cm^{-1}, have been subtracted from the experimental spectrum for better viewing of the MgKr transitions by the reader. Upper-state v' assignments were obtained from isotopic splittings (see text). In the upper-part of the figure are theoretical Franck–Condon intensities calculated from the spectroscopic constants of the upper and lower states listed in Table I.

Under conditions where we were able to record the analogous Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Ar[$^3\Sigma^-$]$\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Ar[$^3\Pi_0$] spectrum[1] with quite high signal-to-noise in the same spectral region, the Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-$]$\leftarrow$Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0$] vibrational transitions shown in Fig. 1 were initially barely discernible from the background noise, and only appeared in the Mg$^+$ channel. In the MgAr case, where most of the R2PI intensity is in the Mg$^+$ channel but some intensity was observed in the MgAr$^+$ channel,[1] it is thought that predissociation occurs to a Mg* state [probably Mg($3s3d$ $^1D_2$)] correlating with a repulsive excited MgAr state.[1] The Mg($3s3d$ $^1D_2$) product state can be one-photon ionized by the visible light which is frequency doubled, and this ''excess'' visible light was allowed to pass into the R2PI chamber along with the UV excitation radiation. We believe that the reason the MgKr transition is so weak is that the net products of Mg($3p\pi3p\pi$ ^3P_J)$\cdot$Kr[$^3\Sigma^-$] predissociation are the Mg($3s3p$ ^3P_J) states, which are in large excess in the beam, of course, and also cannot be one-photon ionized by the ''leftover'' visible light (or even the UV excitation light, for that matter.)

First of all, we know that under essentially identical conditions, Mg($3s3p\pi$ ^3P_J)$\cdot$Kr[$^3\Pi_0$] is definitely present in appreciable concentrations,[11,12] and we confirmed that nothing had changed in the apparatus by again recording, with high signal-to-noise, the $\mathrm{Mg}(3s4s\ ^3S)\cdot\mathrm{Kr}[^3\Sigma^+]\leftarrow\mathrm{Mg}(3s3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Pi_0]$ transitions previously observed and analyzed.[11] The spectra in Fig. 1 were taken with additional radiation at 20 500 cm^{-1} from a second dye laser (pumped by the same XeCl excimer laser pulse). This energy is sufficient to one-photon ionize any Mg excited state produced in the predissociation of the Mg·Kr $^3\Sigma^-$ state which has an energy greater than that of the $\mathrm{Mg}(3s3p\ ^1P_1)$ valence state. The signal-to-noise appeared to be a bit better than without the 20 500 cm^{-1} visible radiation, but not substantially so. We also performed experiments in which we tuned the second dye laser on resonance with the strong $\mathrm{Mg}(3s4d\ ^1D_2)\leftarrow\mathrm{Mg}(3s3p\ ^1P_1)$ atomic transition at 18 083 cm^{-1} to see if $\mathrm{Mg}(3s3p\ ^1P_1)$ was a major predissociation product [the $\mathrm{Mg}(3s4d\ ^1D_2)$ state pumped can, of course, be one-photon ionized by the visible radiation from either dye laser]. This resulted in no discernible enhancement of the signal. We are forced to conclude that the major predissociation product is $\mathrm{Mg}(3s3p\ ^3P_J)$ [or ground-state $\mathrm{Mg}(^1S_0)$, which seems less likely]. The weak signal observed, then, is probably due only to the minor predissociation yield of the more highly excited Mg* states which *can* be one-photon ionized by the visible dye-laser light, and this is the reason it took months rather than days to obtain sufficient signal-to-noise for isotopic-splitting assignments and even confirmation of the source of the spectrum.

As we have pointed out earlier for the analogous $\mathrm{MgAr}(^3\Sigma^-)$ state[1] both "*e*" and "*f*" symmetry rotational levels of the repulsive $\mathrm{Mg}(3s3p\sigma\ ^3P_2)\cdot\mathrm{Kr}[^3\Sigma^+]$ state can couple with the appropriate "*e*" and "*f*" levels of $\mathrm{Mg}(3p\pi_{+1}3p\pi_{-1}\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ $F_1(e)$, $F_2(f)$, $F_3(e)$ levels via spin-other-orbit interactions.[13,14] Since the $\mathrm{MgKr}(^3\Sigma^+)$ state will be more repulsive[15] than the analogous $\mathrm{MgAr}(^3\Sigma^+)$ state, and the $\mathrm{MgKr}(^3\Sigma^-)$ state is more strongly bound than the analogous $\mathrm{MgAr}(^3\Sigma^-)$ state,[1] there may be $^3\Sigma^+/^3\Sigma^-$ curve crossings for MgKr but not for MgAr, rationalizing the apparently almost complete predissociation into $\mathrm{Mg}(3s3p\ ^3P_J)$ product for $\mathrm{MgKr}(^3\Sigma^-)$ but not $\mathrm{MgAr}(^3\Sigma^-)$.[1] The spin-orbit coupling is also likely to be increased by the "heavy-atom-effect" mixing of $\mathrm{Kr}(4p\pi)$ character[7] into the nominally $\mathrm{Mg}(3p\pi_{+1}3p\pi_{-1})$ orbitals in the strongly bound $^3\Sigma^-$ state of MgKr.

The absolute vibrational assignments shown in Fig. 1 were obtained by measurements of the isotopic splittings [isotopic abundances: $^{24}\mathrm{Mg}=78.999\%$, $^{26}\mathrm{Mg}=11.01\%$, $^{84}\mathrm{Kr}=57.0\%$, $^{86}\mathrm{Kr}=17.3\%$] for vibrational bands of $^{24}\mathrm{Mg}^{84}\mathrm{Kr}$ versus $^{26}\mathrm{Mg}^{84}\mathrm{Kr}$ transitions, which were extremely large ($\sim$60 cm^{-1}) for a neutral metal-RG van der Waals state. Shown in Fig. 2 are the experimental isotopic shifts, as well as the isotopic shifts calculated for our vibrational assignments v', versus those calculated for $v'+1$ and $v'-1$. The assignment is certain, despite the fact that the signal-to-noise of the spectra (especially the $^{26}\mathrm{Mg}^{84}\mathrm{Kr}$ bands) were quite low. The $^{24}\mathrm{Mg}^{84}\mathrm{Kr}/^{25}\mathrm{Mg}^{84}\mathrm{Kr}$ isotopic splittings ($\sim$30 cm^{-1}) were also consistent with our v' assignment. Despite the limited signal-to-noise, the main ^{24}MgKr bands, collected in the $^{24}\mathrm{Mg}^+$ channel, showed obvious subband structure (see Fig. 3 for an example), which appears to be due mostly to the large isotopic splittings even for the small reduced mass changes for the Kr isotopic mass variation. The most obvious structure was to the red, and we have assigned each main peak to the most abundant $^{24}\mathrm{Mg}^{84}\mathrm{Kr}$ isotope, and the weaker peak (to the red) to the less abundant $^{24}\mathrm{Mg}^{86}\mathrm{Kr}$ isotope. Shown in Fig. 4 is a plot of the experimental isotopic shifts and those calculated for our assignments v' versus $v'+1$ and $v'-1$. Although the uncertainty (±0.5 cm^{-1}) is large, it can be seen that the "subband" structure is consistent with the expected Kr isotopic splittings, confirming that the spectrum (appearing in the Mg^+ channel only) is due to a transition of the MgKr molecule to a state with unusually high isotopic splittings.

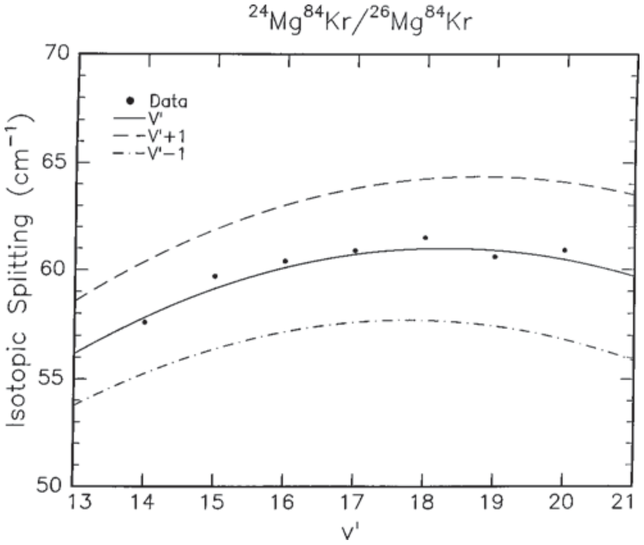

FIG. 2. Dots: Experimental energy differences between transitions to the same v' upper-state level for the $^{24}\mathrm{Mg}^{84}\mathrm{Kr}$ and $^{26}\mathrm{Mg}^{84}\mathrm{Kr}$ isotopomers. The lines shown are the isotopic splittings calculated for our v' assignments versus those for $v'+1$ and $v'-1$ assignments.

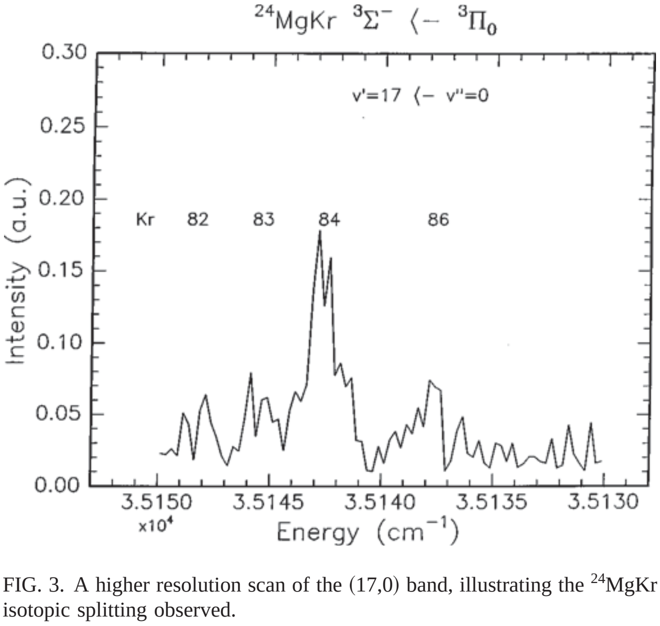

FIG. 3. A higher resolution scan of the (17,0) band, illustrating the ^{24}MgKr isotopic splitting observed.

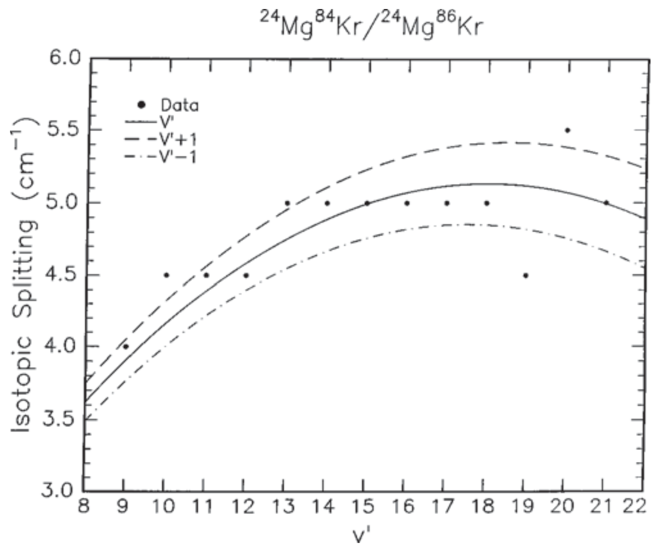

FIG. 4. Dots: Experimental energy differences between transitions to the same v' upper-state level for the ^{24}Mg^{84}Kr versus the ^{24}Mg^{86}Kr isotopomers. The lines shown are the isotopic splittings calculated for our v' assignment versus those for $v'+1$ and $v'-1$ assignments.

Given the absolute v' assignments, a Birge–Sponer plot of $\Delta G'_{1/2}$ vs $v'+1$ was constructed which was quite linear (see Fig. 5). From the slope and the intercept of this plot, $\omega_e'=215.91\pm1.03\ \mathrm{cm}^{-1}$, $\omega_e'x_e'=2.9213\pm0.0312\ \mathrm{cm}^{-1}$, the extrapolated value for $\nu_{0,0}=32\,367\ \mathrm{cm}^{-1}$, and assuming the Birge–Sponer plot is linear all the way to dissociation (which is usually unlikely), $D_e'=(\omega_e')^2/4(\omega_e'x_e')=3994\pm84\ \mathrm{cm}^{-1}$. Another, generally more reliable,[1–4,11,12] estimate for D_e' can be obtained by using the extrapolated $\nu_{0,0}$ value (obtained by assuming the Birge–Sponer plot is linear to $v'=0$, a much more likely possibility), and a thermochemical cycle:

$$D_0'=D_0''(^3\Pi_{0^-})+[E(3p3p\ ^3P_{0,1})-E(3s3p\ ^3P_0)]-\nu_{0,0}$$
$$=(250\pm80)+35\,967-32\,367.$$

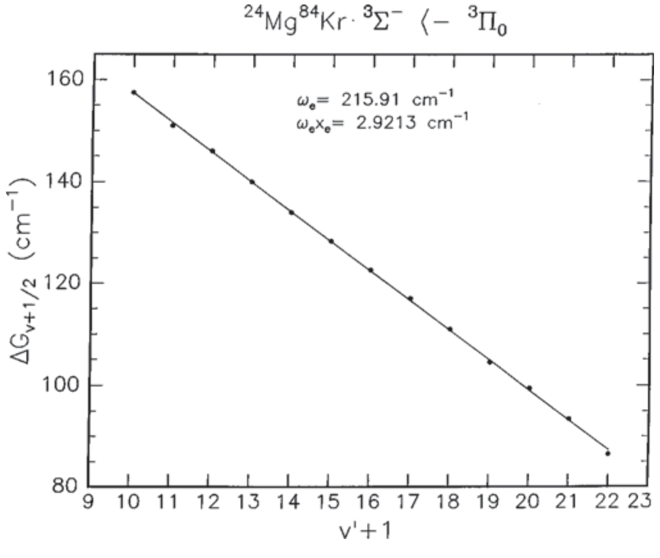

FIG. 5. Birge–Sponer plot of $\Delta G'_{1/2}$ vs $v'+1$ for the transitions shown in Fig. 1.

TABLE I. The ^{24}Mg^{84}Kr band origins for the transition from Mg$(3s3p\pi\ ^3P_J)\cdot$Kr$[^3\Pi_0]$, $v''=0$ to Mg$(3p\pi3p\pi\ ^3P_J)\cdot$Kr$[^3\Sigma^-]$, v', in cm^{-1}.

v'	Band origin
22	35 637.75
21	35 551.25
20	35 457.75
19	35 358.25
18	35 253.75
17	35 142.75
16	35 025.75
15	34 903.25
14	34 774.75
13	34 640.75
12	34 500.75
11	34 354.75
10	34 203.75
9	34 046.75

Thus $D_0'=3859\pm80\ \mathrm{cm}^{-1}$, from which $D_e'=3966\pm80\ \mathrm{cm}^{-1}$, which is actually consistent in this case with the $D_e'=3994\pm84\ \mathrm{cm}^{-1}$ estimate from ω_e' and $\omega_e'x_e'$.

These high values of D_e' are more than twice those expected[16] for any high-*n* Rydberg state of MgKr which could be accessed in this spectral region in absorption from Mg$(3s3p\pi\ ^3P_J)\cdot$Kr$[^3\Pi_0]$ [the Mg$(3s6s)\cdot$Kr state is the only asymptotic possibility], so that assignment of the upper-state as the unusually strongly bound, doubly excited Mg$(3p\pi3p\pi\ ^3P_J)\cdot$Kr$[^3\Sigma^-]$ state is virtually certain.

The signal-to-noise of the spectra were too low to obtain any resolved rotational structure, but we have managed to secure a reasonable estimate of R_e' for the strongly bound upper-state by Franck–Condon simulations, given that $R_e''=3.48\pm0.09$ Å [from several earlier rotationally resolved spectra of transitions from MgKr$(^3\Pi_0)$ to lower-lying MgKr excited states].[11,12] Shown in Fig. 1 (top) is the Franck–Condon intensity distribution obtained from the lower- and upper-state spectroscopic constants listed in Table I, and a ‘‘best-fit’’ value of R_e' of 2.45±0.20 Å. The Franck–Condon maximum is sensitive only to ΔR_e, basically, but the breadth and shape of the vibrational band intensities is determined mainly by ω_e'' (and D_e'') in the ground state, since this is what determines the ‘‘width’’ of the MgKr$(^3\Pi_0,v''=0)$ vibrational wave function. We have previously estimated $D_0''=250\ \mathrm{cm}^{-1}$ for MgKr$(^3\Pi_0)$,[11–13] and we estimate $\omega_e''=33\ \mathrm{cm}^{-1}$ from ω_e'' values for analogous $^3\Pi_0$ states of M·RG states (M=Mg, Zn, Cd, Hg; RG=Ar, Kr).[7] It can be seen that $\omega_e''=33\ \mathrm{cm}^{-1}$ results in a Franck–Condon intensity distribution which is quite consistent with raw experimental peak intensities (which were not normalized to laser excitation intensities, and were obtained with two different dyes, one of which had maximum doubled intensity in the 34 000–34 500 cm^{-1} spectral region of the weaker peaks to the red), but our rough ω_e'' value probably has a $+10\ \mathrm{cm}^{-1}$, $-5\ \mathrm{cm}^{-1}$ uncertainty.

Listed in Table I are the band origins, and in Table II the spectroscopic constants (determined or estimated), for the lower $^3\Pi_{0^-}$ state and the upper $^3\Sigma^-$ state.

TABLE II. Spectroscopic constants for several states of MgKr and $MgKr^+$. All values in cm^{-1}, except R_e, which is in Angstroms.

State	D_e	ω_e	$\omega_e x_e$	R_e
$Mg(3s3p\ ^3P_0)\cdot Kr[^3\Pi_{0^-}]$	$267^{a,b,c}$	$(33)^b$	$(1.02)^b$	3.48 $\pm 0.09^d$
$Mg(3s4s\ ^3S_1)\cdot Kr[^3\Sigma^+]^d$	1736^a	141.3	2.678	2.81 ± 0.05
$Mg(3s3d\ ^3D_J)\cdot Kr[^3\Pi_{0^-}]^e$	621^a	70.0	2.25	3.12 ± 0.06
$Mg(3s3d\ ^3D_J)\cdot Kr[^3\Delta_1]^e$	1931^a	124.7	2.114	2.73 $\pm .09$
$Mg(3p3p\ ^3P_J)\cdot Kr[^3\Sigma^-]^f$	3966^a	215.9	2.921	2.45 ± 0.20
$Mg^+(3s\ ^2S_{1/2})\cdot Kr[^2\Sigma^+]$	$1949^{a,c}$ $(2048)^g$	118^g	$(\sim 1.8)^b$	$(\sim 2.8)^b$
$Mg^+(3p\ ^2P_J)\cdot Kr[^2\Pi_{3/2}]$	$7113^{a,b,g}$ $(7221)^g$	256^g	2.26^g	$(\sim 2.3)^b$

[a] Calculated from our estimate of $D_e = 267\ cm^{-1}$ for the $Mg(3s3p\pi\ ^3P_0)\cdot Kr[^3\Pi_{0^-}]$ state (Ref. 16), the $\nu_{0,0}$ values (or the two-color photoionization threshold values for the $Mg^+\cdot Kr$ states), and thermochemical cycles. Uncertainties are all $\pm 80\ cm^{-1}$.

[b] Our estimates.

[c] Reference 16.

[d] Reference 11.

[e] Reference 12.

[f] This work.

[g] Reference 17.

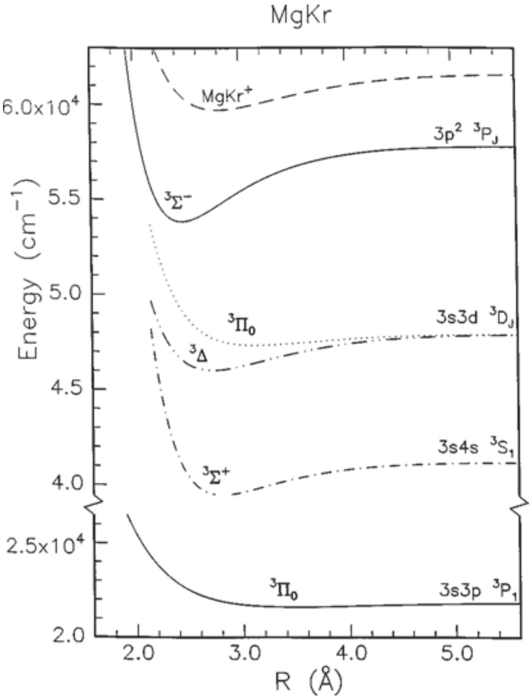

FIG. 6. Morse potential curves of several states of MgKr, and the ground state of $MgKr^+$, calculated from the spectroscopic constants in Table I.

DISCUSSION

The bond energy of the $Mg(3p\pi 3p\pi\ ^3P_J)\cdot Kr[^3\Sigma^-]$ state ($\sim 4000\ cm^{-1}$) is very large for a neutral atom/RG van der Waals state, and in fact, appears to have the greatest bond energy so far determined experimentally for such neutral states (the analogous MgXe state, if we could only detect it, should be even more strongly bound, of course). Perhaps more striking, however, is the fact that this neutral $MgKr(^3\Sigma^-)$ excited state is more than twice as bound as even the $MgKr^+$ ground-state ion,[16,17] where strong ion/induced-dipole forces play the major role in the bonding. Shown in Table II are the spectroscopic constants of all the MgKr and $Mg^+\cdot Kr$ states which have been characterized experimentally to date. [The neutral ground-state, $Mg(3s3s\ ^1S_0)\cdot Kr[^1\Sigma^+]$, has not yet been characterized, but is expected to be very weakly bound, with $D_e < 100\ cm^{-1}$, and $R_e > 4.2$ Å.[7]] Shown in Fig. 6 are Morse potential curves for these Mg*Kr excited states, as well as the $MgKr^+$ ground-state ion.

In our discussion of the bonding in the $Mg(3p\pi 3p\pi\ ^3P_J)\cdot Kr[^3\Sigma^-]$ state, we first point out the huge differences between the D_e, R_e values for the singly excited $Mg(3s3p\pi\ ^3P_J)\cdot Kr[^3\Pi_0]$ state, where $D_e = 267\ cm^{-1}$, and $R_e = 3.48$ Å, versus the doubly excited $Mg(3p\pi 3p\pi\ ^3P_J)\cdot Kr[^3\Sigma^-]$ state, where $D_e = 3966\ cm^{-1}$ is 15 times greater and $R_e = 2.45$ Å is considerably smaller. A similar observation was made earlier for the MgAr states, where the analogous doubly excited $3p\pi 3p\pi\ ^3\Sigma^-$ state was ~ 17 times as bound as the singly excited $3s3p\pi\ ^3\Pi_0$ state: 2960 cm^{-1} versus $\sim 175\ cm^{-1}$, repectively.[1] So what is the simple, main electronic difference between these two states? Both have $3p\pi$ orbitals occupied, which tend to lead to greater bonding than $3p\sigma$ orbital occupation, because the "transverse" $p\pi$ alignment causes substantially less repulsion.[7] But the fundamental difference, we believe, is that the Mg^+ "core" in the singly excited $Mg(3s3p\pi)$ state still has an electron in a $3s$ orbital and this causes insurmountable σ-σ repulsion with the Kr atom to set in at relatively large internuclear distances. On the other hand, the "core" in the $Mg(3p\pi 3p\pi)$ state is $Mg^{++}(2p^6)$, for which the σ-σ repulsion with the Kr atom does not set in until much smaller internuclear distances. [Mg^{++} is tiny compared to Mg^+: the radial expectation value[18] for the $Mg(2p)$ orbital is 0.36 Å, compared to the radial expectation value[18] of the $Mg(3s)$ orbital of 1.72 Å.]

Thus the net σ-σ repulsion is very small at moderate Mg–Kr internuclear distances, and the Kr atom can approach the $Mg(3p\pi 3p\pi)$ atomic state quite closely, allowing all of the possible attractive forces to extend to much shorter distances than for the singly excited $Mg(3s3p\pi)$ atomic state, or even the $Mg^+(3s)$ state. The R_e value for the doubly excited $MgKr(^3\Sigma^-)$ state (2.45 Å) is therefore substantially less than that of the singly exited $MgKr(^3\Pi_0)$ state (3.48 Å) or even the $MgKr^+$ ion (~ 2.8 Å), because the latter two states both have large $Mg(3s)$ orbitals which are singly occupied. [In fact, the $Mg(3p\pi)/Kr(4p\pi)$ repulsion is probably what finally limits the attractive forces at $R_e < 2.4$ Å and determines the small R_e value for the $^3\Sigma^-$ state.]

We now discuss the possible attractive forces[1] which can apparently persist to smaller values of R for the unusual $Mg(3p\pi 3p\pi\ ^3P_J)\cdot Kr[^3\Sigma^-]$ state because of the lack of σ-σ repulsion:

Quadrupole/induced-dipole electrostatic interactions

The $Mg(3p\pi 3p\pi)$ state will have a large $(-)$-(Mg^{++})-$(-)$ quadrupole moment[1] aligned perpendicular to the MgKr axis. This will lead to a substantial induced dipole (as well as higher induced multipoles) on the Kr atom, which will provide large attractive forces. In fact, if the Kr atom approaches the $\mathrm{Mg}(3p\pi 3p\pi)$ state sufficiently closely, it will begin to see a Mg^{++} ''core'' with two excited $3p$ electrons at larger net transverse distances; in the limit this would be a very strong attraction more similar to that of the $\mathrm{Mg}^{++}\cdot\mathrm{Kr}$ ion, where the binding energy should be $>10\,000\ \mathrm{cm}^{-1}$.[1,15]

However, careful high-level *ab initio* calculations we have performed on the analogous $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Ar}[^3\Sigma^-]$ state[19] have shown for that state that purely electrostatic (permanent-quadrupole/induced-multipole) attraction may not be the only attractive force involved. With good basis sets, such an electrostatic *attractive* force should be reasonably represented even at the SCF level, but our calculations indicated that only approximately 30% of the binding energy of $\sim 2900\ \mathrm{cm}^{-1}$ could be generated by SCF calculations[19] (even with the best basis sets.) With high-level correlated calculations, however, we were able to finally generate a binding energy of $\sim 2570\ \mathrm{cm}^{-1}$, or about 87% of the experimental D_e value.[19] This would appear to indicate that electrostatic interactions are not the major attractive force responsible for the strong binding in the doubly excited $\mathrm{MgAr}(^3\Sigma^-)$ state,[1] but we believe it is still an open question as to whether the ''correlation'' contribution can be attributed only to attractive forces but may, in fact, be partially related to ''avoidance'' of repulsion by correlated electron motion. This is a very sophisticated theoretical question, of course, and we hope eventually to examine it in detail after more experimental information on these states is acquired. [Even the idea of separating ''attractive'' and ''repulsive'' forces is arbitrary, and perhaps impossible, as we are well aware, and can even be influenced by one's point-of-view: ''molecular-orbital'' (''chemical'') framework or ''long range forces'' framework for van der Waals attraction, for example.]

''Dispersive'' (van der Waals) attraction

Because the repulsion is so minimal due to the $\mathrm{Mg}(3s)$ orbital being unoccupied, the strongly R-dependent $1/R^6$ long-range dispersive van der Waals forces between the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)$ state and the Kr atom may persist to very short distances R, contributing a great deal to the attraction. Such forces cannot be represented by SCF calculations, of course, and this could also be part of the reason that correlated *ab initio* methods are required to reproduce most of the experimental bond energy.[19] With no outer σ orbitals occupied in the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)$ state, such attractive interaction must presumably involve primarily $\mathrm{Mg}(3p\pi)/\mathrm{Kr}(4p\pi)$ correlated electron motion.

Mixing with MgKr Rydberg states

The high-energy, truly *valence* $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ state is similar in energy to many high-lying, singly excited Rydberg states correlating with atomic $\mathrm{Mg}(3s,nl)$ Rydberg states. It is important to point out that the unusually strong bonding in the $^3\Sigma^-$ state cannot be due to strong mixing of *molecular* Rydberg states $\mathrm{Mg}(3s,nl)\cdot\mathrm{Kr}$ character into the $^3\Sigma^-$ wave function, for two reasons: (a) No singly excited $\mathrm{Mg}(3s,nl)$ Rydberg state can have $^3\Sigma^-$ symmetry, only $^3\Sigma^+$ symmetry.[1] (b) High-energy singly excited states of $\mathrm{Mg}(3s,nl)\cdot\mathrm{Kr}$ character will have bond energies no greater than $\mathrm{Mg}(3s)^+\cdot\mathrm{Kr}$ (e.g., in the limit when the nl Rydberg electron becomes infinitely diffuse),[9,16] so it is obvious that mixing of such Rydberg character into the $^3\Sigma^-$ wave function could not possibly explain why this unusual $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ state is more than twice as strongly bound as the ground-state $\mathrm{Mg}^+\mathrm{Kr}$ ion.

''Chemical'' attraction

It is also possible that there is a weak chemical attraction, formally a Lewis acid/base interaction, whereby the $\mathrm{Ar}(3p\sigma)^2$ filled orbital donates electron density into the empty $\mathrm{Mg}(3s\sigma)$ orbital, forming a weak ''coordinate-covalent,'' σ-type ''chemical'' bond. If this possibility is dominant, then it must be very ''electron-correlation'' dependent, given the results of the *ab initio* calculations of the $\mathrm{MgAr}(^3\Sigma^-)$ potential curve. While we admit that there may be subtle correlation effects in these states which we do not fully understand, we are also skeptical that such ''pseudo-chemical'' interactions can account for the large $\mathrm{MgKr}(^3\Sigma^-)$ van der Waals bond strength.

In fact, it is difficult to distinguish ''chemical'' Lewis acid/base interactions from the polarization of the $\mathrm{Ar}(3p\sigma)$ electrons by the $\mathrm{Mg}(3p\pi 3p\pi)$ quadrupole. The *ab initio* calculations[19] indicate that the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Ar}[^3\Sigma^-]$ state has a large dipole moment of 1.6 Debye, and we have estimated[1] that a dipole moment of ~ 1.5 Debye would be expected just due to the dipole induced on the Ar atom by the quadrupole moment of the $\mathrm{Mg}(3p\pi 3p\pi)$ state at the equilibrium intermolecular distance of 2.4 Å. The dipole moment of the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ state characterized here should be even larger (>2.0 Debye) since the estimated R_e value is about the same, 2.45 Å, and the polarizability of Kr is ~ 1.5 times larger than that of Ar.

Finally, it is interesting to note that although the D_e value of $\sim 4000\ \mathrm{cm}^{-1}$ for the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ state is more than twice that of the $\mathrm{Mg}(3s\ ^2S_{1/2})^+\cdot\mathrm{Kr}[^2\Sigma^+]$ ground-state ion, it is still substantially less than that of its true ionic counterpart, the excited $\mathrm{Mg}(3p\pi\ ^2P_J)^+\cdot\mathrm{Kr}[^2\Pi]$ state[17] which has a D_e value of $\sim 7100\ \mathrm{cm}^{-1}$. This would be the ionic state obtained if one of the $3p\pi$ Mg electrons were removed from the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ state. This ionic excited state also lacks the $\mathrm{Mg}(3s)$ electron, and has only one $\mathrm{Mg}(3p\pi)/\mathrm{Ar}(3p\pi)$ repulsive interaction, but has the added $1/R^4$ ion/induced-dipole force, and should therefore be more strongly bound (and have a shorter bond length) than the $\mathrm{Mg}(3p\pi 3p\pi\ ^3P_J)\cdot\mathrm{Kr}[^3\Sigma^-]$ neutral excited state, as observed.[17]

ACKNOWLEDGMENT

We are grateful to the National Science Foundation for the financial support of this research (Grant No. CHE9628696).

[1] Steven Massick and W. H. Breckenridge, J. Chem. Phys. **105**, 6154 (1996).
[2] John G. Kaup and W. H. Breckenridge, J. Chem. Phys. **107**, 5676 (1997).
[3] Allen W. K. Leung and W. H. Breckenridge (to be published).
[4] Steven Massick and W. H. Breckenridge, Chem. Phys. Lett. **257**, 465 (1996).
[5] R. R. Bennett, J. G. McCaffrey, and W. H. Breckenridge, J. Chem. Phys. **92**, 2740 (1990).
[6] C. T. Scurlock, J. S. Pilgrim, and M. A. Duncan, J. Chem. Phys. **103**, 3293 (1995).
[7] W. H. Breckenridge, C. Jouvet, and B. Soep, in *Advances in Metal and Semiconductor Clusters, Vol. III*, edited by M. Duncan (JIA Press, Greenwich, 1995).
[8] S. Heidecke, S. Fu, J. R. Colt, and M. D. Morse, J. Chem. Phys. **97**, 1692 (1992).
[9] M. Okunishi, K. Yamanouchi, K. Onda, and S. Tsuchiya, J. Chem. Phys. **98**, 2675 (1993); K. Onda, T. Tasaka, A. Hishikawa, and K. Yamanouchi, in *Structures and Dynamics of Clusters* (Univeral Academy Press, Inc., 1996); K. Onda and K. Yamanouchi, J. Chem. Phys. **102**, 1129 (1995).
[10] K. Onda, K. Yamanouchi, M. Okunishi, and S. Tsuchiya, J. Chem. Phys. **101**, 7290 (1994).
[11] John G. Kaup, Allen W. K. Leung, and W. H. Breckenridge, J. Chem. Phys. **107**, 10492 (1997).
[12] John G. Kaup and W. H. Breckenridge, J. Chem. Phys. **107**, 6005 (1997).
[13] X. Yang, L. Pederson, D. R. Yarkony, and P. J. Dagdigian, J. Phys. Chem. **100**, 5649 (1996), and references therein.
[14] H. LeFebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).
[15] J. G. Kaup, S. Bililign, and W. H. Breckenridge, J. Phys. Chem. **99**, 7878 (1995); J. G. Kaup and W. H. Breckenridge, *ibid.* **99**, 13701 (1995).
[16] J. G. Kaup and W. H. Breckenridge, J. Chem. Phys. **107**, 2180 (1997).
[17] J. S. Pilgrim, C. S. Yeh, K. R. Berry, and M. A. Duncan, J. Chem. Phys. **100**, 7945 (1994).
[18] J. P. DesClaux, At. Data Nucl. Data Tables **12**, 311 (1973).
[19] Allen W. K. Leung, Mark Roberson, Jack Simons, and W. H. Breckenridge, Chem. Phys. Lett. **259**, 199 (1996).