Spectroscopic characterization of the Zn\(4s^2\)·Ne\(1\Sigma^+\) and Zn\(4s4p\pi\)·Ne\(1\Pi_1\) van der Waals states


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Abstract

The Zn\(4s^2\)·Ne\(1\Sigma^+\) and the Zn\(4s4p\pi\)·Ne\(1\Pi_1\) states have been characterized by laser-induced fluorescence spectroscopy. Bond lengths were determined from simulations of the partially-resolved rotational structure of the \(1\Pi \leftarrow 1\Sigma^+\) transitions, while bond strengths were estimated from a Birge–Sponer extrapolation with allowance for consistent errors resulting from similar procedures in the analogous Cd·Ne and Hg·Ne transitions. The van der Waals bonding in these states is discussed briefly and compared to that in the analogous M·RG states, where M = Mg, Zn, Cd, Hg and RG = Ne, Ar, Kr, Xe. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Transitions from the M\(ns^2\)·RG\(1\Sigma^+\) ground-state van der Waals complexes to their more strongly-bound M\(nsnp\pi\)·RG\(1\Pi_1\) lowest-lying excited singlet states, where M = Mg, Zn, Cd, Hg and RG = Ne, Ar, Kr, Xe, have all been spectroscopically characterized except for the ZnNe and MgKr molecules [1–7]. It is important that the potential curves of all of these states be determined, both for our general understanding of bonding trends in van der Waals complexes as well as for use as ‘pair-potentials’ in modeling the interactions of metal atoms with more than one rare-gas atom, i.e., in rare-gas clusters [8–11] and solid rare-gas matrices [9–12]. We report here a laser-induced fluorescence (LIF) study of the ZnNe\(1\Pi_1 \leftarrow 1\Sigma^+\) transition, in which the bond lengths and the bond strengths of both the ground and upper states have been determined. Trends in bonding and in spectroscopic constants are discussed for all the analogous M·RG states.

2. Experimental

The apparatus has been described in detail elsewhere [3]. Briefly, Zn vapor in pure Ne gas (\(\sim 9\) atm pressure) was expanded continuously from an oven through a nozzle of \(\sim 0.125\) mm diameter into a vacuum chamber pumped by a Roots system, creating a free supersonic jet expansion. Frequency-doubled light (BBO crystal, Skytek) from an excimer-pumped dye laser was passed into the free jet (via a Pellin–Broca prism system which excluded the visi-
ble dye laser light from the apparatus) to excite ZnNe(\(\Pi_1, v'\)) \(\rightarrow\) ZnNe(\(\Sigma^+, v'' = 0\)) transitions. Fluorescence from the ZnNe(\(\Pi_1, v'\)) states was detected at right angles to both the axis of the expansion and the excitation beam, through a UV band-pass filter (\(\lambda_{\text{max}} = 2180 \, \text{Å}, \text{FWHM} = 230 \, \text{Å}\)), with an Electron-Tubes 9816QB photomultiplier tube operated at 2100 V. The signal from the photomultiplier tube, via a 50 \(\Omega\) termination, was detected with a LeCroy 9310 AM digital-storage oscilloscope over an effective time-interval of \(\sim 50 \, \text{ns}\) which included the laser-excitation pulse. (The fluorescence lifetime of the ZnNe transitions is \(\sim 2 \, \text{ns}\), much shorter than the 15 ns duration of the laser-excitation pulse.) The dye used in the dye laser was Stilbene 420 from Exciton.

3. Results

Shown in Fig. 1 is a laser-induced fluorescence (LIF) spectrum of three bands assigned as ZnNe(\(\Pi_1, v'\)) \(\rightarrow\) ZnNe(\(\Sigma^+, v'' = 0\)) transitions. There is a strong Zn(4s4p \(^3P\), \(J^\pi\)) \(\rightarrow 4s^2\Sigma_g^+\)) atomic transition, centered at 46745.4 \(\text{cm}^{-1}\), due to the large amounts of Zn vapor present, the red wing of which is shown as the rising ‘baseline’ signal from \(\sim 46720\) to \(\sim 46740 \, \text{cm}^{-1}\). The band at \(\sim 46697 \, \text{cm}^{-1}\) has been assigned as the (0, 0) band, based on the following:

1. There is no sign of another band to the red at the expected progression frequency.
2. Computer simulations of the rotational structure of the three bands, including the expected isotopic shifts for all the ZnNe isotopomers, were consistent with the assignment of the band at \(\sim 46697 \, \text{cm}^{-1}\) as the (0, 0) band.

The three bands in Fig. 1 were computer simulated assuming ZnNe(\(\Pi_1, v', J'\)) \(\rightarrow\) ZnNe(\(\Sigma^+, v'' = 0, J''\)) transitions. The line-strengths used for the rotational transitions were those appropriate for saturated transitions. Simulations with normal Hönl–London factors were less successful in reproducing the relative intensities, especially for the P-heads of the more intense (2, 0) and (1, 0) bands, and it appears that the transitions were partially saturated. A laser line-width of 0.16 \(\text{cm}^{-1}\) and a Boltzmann distribution of \(J''\) levels with a temperature of 6.5 K were used in the simulations. Note that the reproducible isotopic structure to the red due to the Zn\(^{28}\)Ne isotopomers (9.2%) is clearly consistent with the assignment of the (1, 0) and (2, 0) bands. In Fig. 2, high-resolution experimental LIF spectra of the (0, 0) and (1, 0) bands are shown along with computer simulations of their rotational structure.
Fig. 3. Potential curves of the Zn(4s): Ne[1Σ⁺] and Zn(4s4pπ): Ne[1Π₂] states \((D' = 27 \text{ cm}^{-1}, D'' = 81 \text{ cm}^{-1})\).

Spectroscopic constants for the upper and lower states derived from the simulations are shown in Table 1. No hot bands were observed (even though \(v'' = 1, 2\) levels should exist), and \(\omega_x = 15 \pm 3 \text{ cm}^{-1}\) was estimated from ground-state \(\omega_x\) values for the analogous MgNe, CdNe, and HgNe ground states (see Table 2). Shown in Fig. 3 are the Morse potential curves determined for the Zn 4s Ne \(\Sigma^+\) and Zn(4s4pπ)Ne(1Π₂) states. An ab initio calculation of the Zn(4s²)Ne(1Σ⁺) state has yielded \(D' = 15 \text{ cm}^{-1}\); \(R_\epsilon = 4.4 \text{ Å}\) [11]. Such calculations are difficult, and routinely underestimate \(D\) values and overestimate \(R\) values [14–16], so the ab initio results [13] are quite consistent with our experimentally derived values of \(D'\) and \(R\).

In the analogous CdNe and HgNe molecules, where the \(1\Sigma⁺\) ground-state \(D'\) values are accurately known \((\pm 2 \text{ cm}^{-1})\) from direct determinations of the dissociation limits of weakly-bound excited triplet states [1], Birge–Sponer extrapolation of the \(1\Pi – 1\Sigma^+\) vibrational progressions in those cases underestimate the true \(D''\) value of the \(1\Sigma^+\) state (and the \(D'\) value of the \(1\Pi_1\) state, of course), by \(\sim 11\) and \(\sim 8 \text{ cm}^{-1}\), respectively. We thus believe our derived \(D'\) and \(D''\) values may be as much as \(10 \text{ cm}^{-1}\) too low. Also, the \(\omega_x, x^e\) value for the ZnNe(1Π₁) state is based on only three bands, and may be uncertain to \(\pm 0.2 \text{ cm}^{-1}\), yielding an experimental uncertainty in \(D'\) of \(\pm 3 \text{ cm}^{-1}\). We therefore quote \(D'\) and \(D''\) for the ZnNe states with the reasonable error limits of \(\pm 12\) and \(\pm 3 \text{ cm}^{-1}\), respectively. Based on the CdNe and HgNe cases, we estimate that the true \(D'\) and \(D''\) values for the ZnNe states are probably \(\sim 81\) and \(\sim 27 \text{ cm}^{-1}\), respectively.

Table 1

<table>
<thead>
<tr>
<th>Spectroscopic constants for ⁴⁴Zn²⁰Ne states (all units in cm⁻¹ except (R_u, R_e), which are in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_u) (= 20 \text{ cm}^{-1}, 10.3 \text{ cm}^{-1})</td>
</tr>
<tr>
<td>(D'' = 27 \text{ cm}^{-1}, 18 \text{ cm}^{-1})</td>
</tr>
<tr>
<td>(\omega_x = 15 \pm 3 \text{ cm}^{-1})</td>
</tr>
<tr>
<td>(\omega_x, x^e)</td>
</tr>
<tr>
<td>(B_u = 0.0002 \pm 0.0003)</td>
</tr>
<tr>
<td>(B_e = 0.0760 \pm 0.0030)</td>
</tr>
<tr>
<td>(\alpha = 9.1 \times 10^{-3})</td>
</tr>
<tr>
<td>(R_u = 4.29 \pm 0.10)</td>
</tr>
<tr>
<td>(r_{0,0} = 3.56 \pm 0.06)</td>
</tr>
<tr>
<td>(r_{1,1} = 4.6718.0)</td>
</tr>
</tbody>
</table>

\(a\) From \(\Delta'\) of \(1\Pi_1\) state, and a thermochemical cycle.
\(b\) From a Birge–Sponer extrapolation.
\(c\) \(\omega_x\) value estimated from values of analogous MgAr, CdAr, HgAr states (see Table 2).
\(d\) Derived from \(B_u\) only.  
\(e\) Estimated from Morse potential assuming \(D' = 27 \text{ cm}^{-1}\).
\(f\) Our ‘best estimate’ (see text).
\(g\) If \(\Delta' = 27 \text{ cm}^{-1}\), \(\omega_x = 15 \text{ cm}^{-1}\), then \(\omega_x, x^e = \omega_x^2 / 4\Delta' = 2.1 \text{ cm}^{-1}\) (Morse potential).
Table 2

Spectroscopic constants $D_v, \omega_v, R_e$ for M–RG states ($D_v, \omega_v$ values in cm$^{-1}$; $R_e$ values in Å; estimated values in brackets)

<table>
<thead>
<tr>
<th>State of M atom</th>
<th>Molecular electronic state</th>
<th>$D_v$</th>
<th>$\omega_v$</th>
<th>$R_e$</th>
<th>$D_v$</th>
<th>$\omega_v$</th>
<th>$R_e$</th>
<th>$D_v$</th>
<th>$\omega_v$</th>
<th>$R_e$</th>
<th>$D_v$</th>
<th>$\omega_v$</th>
<th>$R_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (5s$^2$3p$^1$)</td>
<td>$^1\Sigma^+$</td>
<td>23 ± 5$^e$</td>
<td>14.0 ± 0.5$^e$</td>
<td>4.40 ± 0.15$^b, k$</td>
<td>24.1 ± 1.0$^b$</td>
<td>4.49 ± 0.10$^b$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>94 ± 80$^c$</td>
<td>–</td>
<td>4.56 ± 0.15$^b$</td>
<td></td>
</tr>
<tr>
<td>Zn (4s$^2$3p$^1$)</td>
<td>$^1\Sigma^+$</td>
<td>23 ± 5$^e$</td>
<td>15 ± 3$^e$</td>
<td>4.16$^b, k$</td>
<td>22 ± 3$^f$</td>
<td>4.18 ± 0.07$^f$</td>
<td>[110 ± 40]$^b, k, l$</td>
<td>[13.5]$^b$</td>
<td>4.20 ± 0.10$^b$</td>
<td>162 ± 2$^i$</td>
<td>13 ± 2$^i$</td>
<td>[4.4]$^b, l$</td>
<td></td>
</tr>
<tr>
<td>Cd (5s$^2$3p$^1$)</td>
<td>$^1\Sigma^+$</td>
<td>39 ± 2$^e$</td>
<td>13 ± 1$^e$</td>
<td>4.26 ± 0.10$^e$</td>
<td>107 ± 2$^e$</td>
<td>19 ± 1$^e$</td>
<td>4.31 ± 0.06$^e$</td>
<td>130 ± 2$^e$</td>
<td>17 ± 1$^e$</td>
<td>–</td>
<td>183 ± 2$^e$</td>
<td>–</td>
<td>a</td>
</tr>
<tr>
<td>Hg (6s$^2$3p$^1$)</td>
<td>$^1\Sigma^+$</td>
<td>46 ± 2$^e$</td>
<td>18.5 ± 1.0$^o$</td>
<td>3.90 ± 0.02$^o$</td>
<td>142 ± 2$^e$</td>
<td>23.5 ± 1.0$^o$</td>
<td>3.99 ± 0.01$^o$</td>
<td>178 ± 2$^e$</td>
<td>20 ± 1$^o$</td>
<td>[4.07]$^b, c$</td>
<td>254 ± 2$e$</td>
<td>18 ± 1$^i$</td>
<td>[4.25]$b, c$</td>
</tr>
<tr>
<td>Mg (3s$^2$3p$^1$)</td>
<td>$^1\Pi$</td>
<td>53 ± 6$^b$</td>
<td>21.3 ± 1.2$^b$</td>
<td>3.9$^b$</td>
<td>368 ± 30$^b$</td>
<td>43 ± 1$^b$</td>
<td>3.27 ± 0.05$^b$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1500 ± 80$^c$</td>
<td>97.5 ± 1.0$^b$</td>
<td>3.07 ± 0.10$^e$</td>
</tr>
<tr>
<td>Zn (4s$^2$4p$^1$)</td>
<td>$^1\Pi$</td>
<td>81 ± 2$^c$</td>
<td>25.8 ± 0.4$^d$</td>
<td>3.48 ± 0.06$^d$</td>
<td>706 ± 40$^c$</td>
<td>62 ± 1$^c$</td>
<td>2.97 ± 0.03$^c$</td>
<td>1466 ± 50$^c$</td>
<td>81 ± 1$^c$</td>
<td>2.79 ± 0.03$^c$</td>
<td>3341 ± 100$^c$</td>
<td>117 ± 2$^c$</td>
<td>[2.8]$^c$</td>
</tr>
<tr>
<td>Cd (5s$^2$4p$^1$)</td>
<td>$^1\Pi$</td>
<td>89 ± 2$^e$</td>
<td>23.5 ± 1.0$^e$</td>
<td>3.61 ± 0.06$^e$</td>
<td>544 ± 10$^e$</td>
<td>48 ± 1$^e$</td>
<td>3.28 ± 0.03$^e$</td>
<td>1036 ± 40$^e$</td>
<td>57 ± 1$^e$</td>
<td>–</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Hg (6s$^2$4p$^1$)</td>
<td>$^1\Pi$</td>
<td>97 ± 2$^e$</td>
<td>27 ± 1$^e$</td>
<td>3.41 ± 0.02$^e$</td>
<td>542 ± 10$^e$</td>
<td>50.3 ± 0.2$^e$</td>
<td>3.28 ± 0.08$^e$</td>
<td>1495 ± 40$^e$</td>
<td>69.1 ± 1.0$^e$</td>
<td>[2.93]$^b, c$</td>
<td>3595 ± 800$^{c, i}$</td>
<td>99 ± 10$^{c, i}$</td>
<td>[2.95] ± 0.15$^{c, i}$</td>
</tr>
</tbody>
</table>

$^a$Excited state predissociates rapidly.
$^b$'Kong's rule' estimate of ground-state $R_e$ values; excited state estimates by Franck–Condon simulations, given the ground-state estimates.
$^c$Ref. [1].
$^d$This Letter.
$^e$Ref. [2].
$^f$Ref. [3].
$^g$Ref. [4].
$^h$Ref. [5].
$^i$Ref. [6].
$^j$Ref. [7]; only 3 bands at very high $\epsilon'$ were observed, so we believe the $^1\Pi_1$ state spectroscopic values are quite uncertain.

"Our 'best estimate'.
4. Discussion

As can be ascertained from Table 2, the ZnNe molecule follows a general trend for the M·RG states. The ground $^1\Sigma^+$ state of Zn·Ne is quite weakly bound, $D_e' \approx 27$ cm$^{-1}$, with a large bond distance, $R_e' \approx 4.16$ Å, while the Zn(4s4p$\pi$)·Ne($^3\Pi_1$) excited state is much more strongly bound, $D_e' \approx 81$ cm$^{-1}$, and has a shorter bond length, $R_e' \approx 3.48 \pm 0.06$ Å. As the Ne atom approaches the Zn(4s$^2$) filled sub-shell, the small dispersive attraction at large $R$ is soon overcome by Zn(4s$^2$)/Ne(2p$\sigma^2$) exchange repulsion, resulting in a weak $^1\Sigma^+$ ground-state van der Waals bond. In contrast, in the $^3\Pi_1$ excited state, the Ne approaches the highest-energy Zn(4p$\pi$) electron along its nodal axis [1], with little initial repulsion. At large $R$, in addition to Zn(4p$\pi$)/Ne(2p$\pi$) and Zn(4s)/Ne(2p$\sigma$) dispersive attraction, there is an attractive interaction with the large, perpendicular quadrupole moment of the Zn(4s4p$\pi$) state (quadrupole/induced-dipole being the longest range term). At shorter distances, where $R$ is comparable to or smaller than the 'size' of the quite diffuse excited Zn(4p$\pi$) orbital, the Ne atom begins to experience an attractive 'ion/induced-dipole' type force which would approach that of the Zn(4s$^2$)/Ne ground-state ion if there were no Zn(4p$\pi$)/Ne(2p$\sigma$) repulsion.

As seen in Table 2, the M·RG bond energies (both ground- and excited-state) increase in the order Ne < Ar < Kr < Xe for a given M, because all of the attractive forces increase with the polarizability of the RG atom (in Å$^3$) [17]: Ne, 0.396; Ar, 1.64; Kr, 2.48; and Xe, 4.04. There is a particularly large increase from Ne to Ar, since there is a four-fold increase in polarizability. On the other hand, the effective 'hard-sphere' radii (in Å) [18] of the RG atoms do not increase so rapidly: Ne, ~ 1.4; Ar, ~ 1.7; Kr, ~ 1.8; Xe, ~ 2.0, so the increase in attractive forces with polarizability of the RG atom is greater than the increase in the repulsive forces at intermediate distances $R$, and the bond strengths thus increase in the order Ne < Ar < Kr < Xe. This is especially obvious for the more strongly-bound $^3\Pi_1$ states, where despite the increase in RG atom 'size' the bond lengths (when known) actually decrease substantially in the order Ne > Ar > Kr, as the bond strengths increase rapidly in the same order.

These same kinds of trends are observed for the $D_e$ and $R_e$ values of the analogous ground-state M(ns)$^+$/RG ions. For example, for the Mg(3s)$^+$/RG states, where RG = Ne, Ar, Kr, the $D_e$ values increase substantially (200, 1290, 1949 cm$^{-1}$, respectively [15,16,19]) while the $R_e$ values decrease slightly (~ 3.15, 2.80, ~ 2.8 Å, respectively [19–21])

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References