Potential energy curves of $M(np^2P)\cdot RG(^2II)$ excited states and $M^+\cdot RG$ ground states ($M=$Li, Na; RG=He, Ne)

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It has been established for some time that the bond energies for any given valence $p\pi$ excited state of Group 1 ($^2P$) and Group 2 ($^1\text{P}_3/2$) metal-atom/rare-gas (M-RG) van der Waals complexes tend to increase with the polarizability of the RG atom. It is also known that the binding energies of the corresponding $M^+\cdot RG$ ground state ions are generally greater than those of the neutral $M(p\pi)\cdot RG$ excited states with the same RG atom. However, there are two stark exceptions to these trends, both involving Group 1 metal atoms and the rare gas He; Li($2p^2P\cdot He(^2II)$ and Na($3p^2P\cdot He(^2II)$, which are the focus of the present study. We have conducted ab initio calculations of the potential energy curves of $M(np^2P)\cdot RG(^2II)$ and $M^+\cdot RG$ states, where $M=$Li, Na and RG=He, Ne. We find that the unusual behavior of the $p\pi$ Group 1 metal atom states is due to (i) the lack of $M(p\pi)\cdot RG(p\pi)$ repulsive orbital overlap in the He case, and (ii) substantial additional attraction due to correlated motion of the RG atom's electrons and the diffuse $M(np\pi)$ electron which is absent in the $M^+\cdot RG$ cases.

I. INTRODUCTION

Many excited electronic states of metal-atom/rare-gas (M-RG) van der Waals complexes have now been characterized experimentally. An interesting class of such complexes are those of Group 1, 2, and 12 metal atoms in which a ground-state $ns$ electron has been excited (experimentally, usually by laser excitation) to a valence $np$ orbital.1-49 The binding character of the $M(np)\cdot RG$ or $M(nsnp)\cdot RG$ excited states depends dramatically on the alignment of the $np$ orbital with respect to the internuclear axis. Sigma alignment of the $np$ orbital is more favorable at very long range, where the axial $np\sigma$ electron density provides a greater dispersive attraction. However, $M(np\sigma)\cdot RG(\sigma)$ electron-repulsion also sets in at very large distances; therefore the $M(np\sigma)\cdot RG$ and $M(nsnp\pi)\cdot RG$ states are essentially repulsive but have very shallow potential minima at large $R_e$ values. In contrast, for $pi$ alignment of the $M(np)$ orbital, because the RG atom is approaching along the $np\pi$ orbital nodal axis, electron-electron repulsion does not become appreciable until much smaller values of $R$. The RG atom can thus penetrate much closer to the $M^+$ core and experience strong ion-induced-dipole-like attractive forces. Therefore, the $M(np\pi)\cdot RG$ and $M(nsnp\pi)\cdot RG$ states are more strongly bound.

Shown in Table I are $R_e$ and $D_e$ data for a series of such complexes.1-49 Included for comparisons are similar values for analogous ground-state $M^+\cdot RG$ complexes for which $R_e$ and $D_e$ have either been estimated experimentally or calculated by ab initio techniques. There are two clear trends in $D_e$ values, which can be discerned from the $\pi$ state and $M^+\cdot RG$ data in Table I.

First, for a given metal atom state, the $D_e$ values tend to increase in the order He, Ne, Ar, Kr, Xe. This is expected, of course, since the polarizability of the RG atom increases in this order, and any attractive interaction $[M(p\pi)\cdot RG$ dispersion, $M^+(core)\cdot RG$ ion-induced-dipole, etc.] will increase with RG polarizability. Analogous trends are also observed in $M$-RG ground state $D_e$ values, and in excited $M^+(RG)$ $D_e$ values.50 However, there are two glaring exceptions, both for Group 1 metal atoms with RG=He: Li($2p^2P\cdot He(^2II)$ and Na($3p^2P\cdot He(^2II)$, (see Table I). The second clear trend is that the $D_e$ values for $M^+\cdot RG$ ions are greater than for the analogous valence $p\pi$ excited $M$-RG states. This trend makes sense, since in the neutral $\pi$ states, the $np\pi$ electron is partially shielding the $M^+$ core. However, there are two exceptions to this trend, again involving Li($2p^2P\cdot He(^2II)$, and Na($3p^2P\cdot He(^2II)$ (see Table I). The unexplained high binding energies of the valence $np\pi$ states of Li-He and Na-He is quite interesting and was the basis of the work reported here. As detailed below, we find that the exceptional behavior apparently has to do both with He being the RG atom as well as the Group 1 nature of Li and Na, since the $np\pi$ excited states of Mg-He (Group 2) and Hg-He (Group 12) complexes, for example, are less bound than the analogous complexes for RG=Ne. (See Table I.) We also note particularly the astounding difference in the $D_e$ values for the $p\pi$ state of Na-He($^2II$) ($\sim 490 \text{ cm}^{-1}$) compared to the analogous $p\pi$ state of Mg-He($^2II$) ($\sim 15 \text{ cm}^{-1}$)!

The binding differences between the excited $p\pi$ $M\cdot RG$ states of Group 1 versus Group 2, 12 metal atoms is easy to rationalize qualitatively.50 The $M^+$ cores of Group 1 $np\pi$ states are very small compared to their group 2 or group 12 analogs, which have an $ns$ valence orbital occupied. For example, the mean radius of a $3s$ electron in the Mg atom is 1.72 Å, compared to the mean radius of a Na$^+$ ion of only 0.42 Å. This means that a He atom can penetrate much closer to the $M^+$ core for, say, the Na($3p\pi$) state than for the...
Table I. M-RG valence excited states and M⁺-RG ground states. (M=Group 1, 2, 12 metal atoms; RG=rare gas atoms.) D_e values in cm⁻¹; R_e values in Å.

<table>
<thead>
<tr>
<th>Metal atom atomic state</th>
<th>Molecular state</th>
<th>M-He</th>
<th>M-Ne</th>
<th>M-Ar</th>
<th>M-Kr</th>
<th>M-Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(2p 2P_3/2)</td>
<td>3Σ⁺</td>
<td>1020</td>
<td>1.78</td>
<td>212</td>
<td>2.31</td>
<td>[800]</td>
</tr>
<tr>
<td>Li⁺(1s₂ 1S₁)</td>
<td>2Σ⁺</td>
<td>[596]</td>
<td>[1.96]</td>
<td>[920]</td>
<td>[2.11]</td>
<td>[2173]</td>
</tr>
<tr>
<td>Na(3p 2P_3/2)</td>
<td>3Σ⁻</td>
<td>[570]</td>
<td>[1.96]</td>
<td>[968]</td>
<td>[2.06]</td>
<td>[2195]</td>
</tr>
<tr>
<td>Be⁺(1s² 2S₂)</td>
<td>2Σ⁺</td>
<td>[593]</td>
<td>[1.93]</td>
<td>[1034]</td>
<td>[1.99]</td>
<td>[2520]</td>
</tr>
<tr>
<td>Mg(3s³ 2P_3)</td>
<td>3Π₁</td>
<td>[601]</td>
<td>[1.92]</td>
<td>[1001]</td>
<td>[2.04]</td>
<td>[2040]</td>
</tr>
<tr>
<td>Mg⁺(3s² 2S₁)</td>
<td>2Σ⁺</td>
<td>[868]</td>
<td>[1.81]</td>
<td>(1001)</td>
<td>(2.04)</td>
<td>(2190)</td>
</tr>
<tr>
<td>Mg⁺(3s³ 2Σ⁺)</td>
<td>2Σ⁺</td>
<td>1144</td>
<td>2.73</td>
<td>568</td>
<td>2.91</td>
<td>760</td>
</tr>
<tr>
<td>Mg⁺(3s³ 2Σ⁻)</td>
<td>2Σ⁻</td>
<td>4.55</td>
<td>7.99</td>
<td>568</td>
<td>2.91</td>
<td>760</td>
</tr>
<tr>
<td>Na⁺(2p 1S₀)</td>
<td>2Σ⁺</td>
<td>[480]</td>
<td>[2.3]</td>
<td>(1001)</td>
<td>(2.04)</td>
<td>(2190)</td>
</tr>
<tr>
<td>Na⁺(2p 1S₀)</td>
<td>2Σ⁻</td>
<td>(496)</td>
<td>(2.30)</td>
<td>(1001)</td>
<td>(2.04)</td>
<td>(2190)</td>
</tr>
<tr>
<td>Zn⁺(4s² 2P_3)</td>
<td>3Π₂</td>
<td>[868]</td>
<td>[1.81]</td>
<td>(1001)</td>
<td>(2.04)</td>
<td>(2190)</td>
</tr>
<tr>
<td>Zn⁺(4s² 2P_3)</td>
<td>3Π₁</td>
<td>[480]</td>
<td>[2.3]</td>
<td>(1001)</td>
<td>(2.04)</td>
<td>(2190)</td>
</tr>
<tr>
<td>Cd⁺(5s₀ 2P_3)</td>
<td>3Π₁</td>
<td>322</td>
<td>3.46</td>
<td>322</td>
<td>3.46</td>
<td>322</td>
</tr>
<tr>
<td>Cd⁺(5s₀ 2P_3)</td>
<td>3Π₁</td>
<td>322</td>
<td>3.46</td>
<td>322</td>
<td>3.46</td>
<td>322</td>
</tr>
<tr>
<td>Hg⁺(6s 2P_3)</td>
<td>3Π₁</td>
<td>435</td>
<td>3.37</td>
<td>435</td>
<td>3.37</td>
<td>435</td>
</tr>
</tbody>
</table>

Table I is from a theoretical calculation of potential curve.

\[ D_e = \text{Prob. upper limit: Possible maxima in } 3Σ⁺ \text{ or } 3Σ⁻ \]
\[ R_e = \text{Estimated value, a value which has been determined indirectly, or a value which is relatively uncertain, we believe.} \]

One aspect of the \( D_e \) and \( R_e \) trends that is difficult to explain is why, when interacting with np M atom states, the Ne atom yields so much larger \( R_e \) values than the He atom even though the Ne atom is not that much larger than the He atom. For example, the mean radius of the 1s electrons in He...
We report here ab initio calculations of the potential curves of the Li(2p \(^2P\))·He(\(^2\)S\(^+)\)) and Na(3p \(^2P\))·He(\(^2\)S\(^+)\)) states, and for comparison, the potential curves of the Li\(^+(1s^2 \Sigma^+\))·He(\(^1\Sigma^+\)) and Na\(^+(2p^6 \Sigma^+)\)·He(\(^1\Sigma^+\)) ionic states. Calculations with the Ne atom replacing the He atom were also carried out (or have been performed by others\(^{10}\)). The results of these calculations, our analysis of them, and a discussion of van der Waals bonding in such M·RG and M\(^+-\)RG states, are presented.

### II. THEORETICAL METHODOLOGY

The electronic ground states of closed-shell \(\text{Li}^+\)·He, \(\text{Na}^+\)·He, and \(\text{Na}^+\)·Ne ions were described by the quadratic configuration interaction including single and double excitations with approximate treatment of triple excitations based on a self-consistent field (SCF) reference function [QCISD(T)], implemented via the GAUSSIAN 92 code.\(^{53}\) All valence electrons were correlated. For \(\text{Li}^+\)·Ne, a high quality potential curve was available,\(^{10}\) so we merely verified its accuracy.

The first \(^2\)II excited states (\(^3\)\(B_1\) in \(C_{2v}\) symmetry) of \(\text{Li}^+\)·He, \(\text{Na}^+\)·Ne, \(\text{Na}^+\)·He, and \(\text{Na}^+\)·Ne were described by complete active space (CAS) self-consistent field (SCF) multifreference configuration interaction (MRCI) wave functions, implemented via the GAMESS code.\(^{54}\) The constitution of the configuration spaces used is given in Table II. The basis sets used for each calculation are listed in Table III.\(^{55-64}\) The QCI and MCSCF/MRCI interaction energies were corrected for the basis set superposition error using the function counterpoise procedure,\(^{65}\) and the MCSCF/MRCI interaction energies were corrected for size-inconsistency error by using the supermolecule to compute the asymptotic energies.\(^{66}\)

All of the ab initio calculations were performed on our IBM RISC System 6000 350 workstations.

### TABLE II. Constitution of the MCSCF/MRCI wave function.

<table>
<thead>
<tr>
<th>Species</th>
<th>FC(^*)</th>
<th>Active(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiHe</td>
<td>1(\sigma)(_\text{Li})</td>
<td>1(\sigma)(<em>\text{He}), 2(\sigma)(</em>\text{Li}), 2(\rho)(_\text{Li})</td>
</tr>
<tr>
<td>LiNe</td>
<td>1(\sigma)(<em>\text{Li}), 1(\sigma)(</em>\text{Ne})</td>
<td>2(\sigma)(<em>\text{Ne}), 2(\rho)(</em>\text{Ne}), 2(\pi)(<em>\text{Li}), 2(\rho)(</em>\text{Li})</td>
</tr>
<tr>
<td>NaNe</td>
<td>1(\sigma)(<em>\text{Ne}), 1(\sigma)(</em>\text{Na}), 2(\sigma)(<em>\text{Na}), 2(\rho)(</em>\text{Ne})</td>
<td>2(\sigma)(<em>\text{Ne}), 2(\rho)(</em>\text{Ne}), 3(\sigma)(<em>\text{Na}), 3(\rho)(</em>\text{Na})</td>
</tr>
<tr>
<td>NaHe</td>
<td>1(\sigma)(<em>\text{Ne}), 2(\sigma)(</em>\text{Ne}), 2(\rho)(_\text{Ne})</td>
<td>1(\sigma)(<em>\text{He}), 3(\sigma)(</em>\text{Na}), 3(\rho)(_\text{He})</td>
</tr>
</tbody>
</table>

\(^{*}\)Frozen core orbitals, i.e., orbitals which are doubly occupied in every configuration state function.

\(^{b}\)Orbitals among which the valence electrons are distributed in all possible ways to form a reference space for the CI (single and double excitation) calculation.

is 0.49 Å, while that of the 2\(p\) electrons in Ne is only 0.51 Å.\(^{51}\) Also, estimates of the “hard-sphere” radius of the helium atom are \(\sim 1.3\) Å vs \(\sim 1.4\) Å for the neon atom.\(^{52}\) Finally, as shown in Table I, when the \(np\) orbital is empty, the estimated \(R_e\) values for the \(\text{Li}^+\)·He and \(\text{Na}^+\)·He ions are not much smaller than the \(R_e\) values for the \(\text{Li}^+\)·Ne and \(\text{Na}^+\)·Ne ions, respectively. Another aspect that is not easy to rationalize is why \(\text{Na}(3p \ ^2P)\)·He(\(^2\)\(1\)\(S\)) and \(\text{Li}(2p \ ^2P)\)·He(\(^2\)\(1\)\(S\)) are even more strongly bound, and have shorter \(R_e\) values, than \(\text{Na}^+\)·He and \(\text{Li}^+\)·He, as seen in Table I.

The resolution of both of the above questions suggested by the data obtained in this study is that (i) repulsion between the diffuse M(\(np\)\(_T\)) electron and the RG atom is very small for He but not so for Ne, and (ii) there exist attractive dispersive interactions between the M(\(np\)\(_T\)) electron and the He or Ne atom’s electrons that are absent in the M\(^+-\)RG cases. The balance that is established between attractive and repulsive interactions leads to a shorter \(R_e\) and larger \(D_e\) for MHe(\(^2\)\(1\)\(S\)) than for MNe(\(^2\)\(1\)\(S\)), primarily because of the significantly weaker repulsion in MHe(\(^2\)\(1\)\(S\)). This balance leads to smaller \(R_e\) and larger \(D_e\) values for MHe(\(^2\)\(1\)\(S\)) than for MHe because of the dispersive attraction present in the MHe(\(^2\)\(1\)\(S\)) cases.

### TABLE III. Basis sets used in the ab initio calculations.

<table>
<thead>
<tr>
<th>System</th>
<th>State</th>
<th>Basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)He</td>
<td>(^1\Sigma^+)</td>
<td>6-311G* plus three (p) (He) and three (d) (Li); splitting factors (4,1,0.25),(^b) exponents 0.75 ((p)), 0.2 ((d))</td>
</tr>
<tr>
<td>LiHe</td>
<td>(^3\Pi)</td>
<td>DZV(^b) with one (p) (0.076) on Li and one (d) (1.883) on Ne(^f)</td>
</tr>
<tr>
<td>Li(^+)Ne</td>
<td>(^3\Sigma^+)</td>
<td>6-311 G**(^e)</td>
</tr>
<tr>
<td>Na(^+)He</td>
<td>(^3\Sigma^+)</td>
<td>Ne: as in (\text{Li}^+)·Ne; Na: HW(^f) plus one (p) (0.061)</td>
</tr>
<tr>
<td>LiNe</td>
<td>(^1\Pi)</td>
<td>SBK(^f) plus two (d) on Ne (0.852, 4550)(^g) plus four diffuse (d)'s on Li, exponents 0.9, 0.2723, 0.0842, 0.0210(^i)</td>
</tr>
<tr>
<td>NaHe</td>
<td>(^3\Pi)</td>
<td>He: as in LiHe; Ne: 6-311 G plus three (d); exponent 0.175, splitting factors (4,1,0.25),(^h)</td>
</tr>
<tr>
<td>NaNe</td>
<td>(^3\Pi)</td>
<td>TZV(^h) plus three (d); splitting factors (4,1,0.25), exponents 2.0 (Ne) and 0.157 (Na)(^i)</td>
</tr>
<tr>
<td>Li(^+)Ne</td>
<td>(^2\Delta)</td>
<td>As in LiNe ((^3)(\Pi))</td>
</tr>
</tbody>
</table>

\(^a\)Reference 55.
\(^b\)Reference 62.
\(^c\)Reference 57.
\(^d\)Reference 59.
\(^e\)Reference 58.
\(^f\)Reference 56.
\(^g\)Reference 61.
\(^h\)Reference 60.
\(^i\)Reference 64.

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II. RESULTS AND DISCUSSION

A. Comparing $^2 \Pi$ states of M-RG to the ground states of M$^+$RG

Shown in Figs. 1-4 are potential curves calculated for the $^2 \Pi$ excited states of the van der Waals molecules of interest and the corresponding ground-state cations. The fact that neutral LiHe and NaHe are more strongly bound than their corresponding cations while LiNe and NaNe are less strongly bound than their cations is strikingly illustrated in these figures.

Shown in Table IV are $D_e$ and $R_e$ values extracted from our calculations, along with similar values from earlier experimental and theoretical studies for comparison purposes. It can be seen that our calculated $R_e$ and $D_e$ values are reasonably consistent with both the experimental estimates and with the findings of other ab initio calculations. In fact, our calculated results in some cases may be only in fortuitously good agreement with the experimental data given the modest basis sets and configuration spaces employed, but the main purpose of our calculations is to obtain a qualitative understanding of the bonding in these states.

The fact that the $R_e$ values for Li$^+$He vs Li$^+$Ne (and Na$^+$He vs Na$^+$Ne) agree within ~0.1 Å (see Table IV), as do the He and Ne hard sphere radii, indicates that the intrinsic "size" of Ne is not much larger than that of He, as stated earlier. When interacting with the closed-shell cations (Li$^+$ and Na$^+$), the He and Ne atoms behave as though their sizes are quite similar, so the intrinsic sizes of the rare gas atoms are not what causes M-He($^2 \Pi$) to be more strongly bound than MNe($^2 \Pi$).

B. Origin of the strong binding in the Li-He($^2 \Pi$) and Na-He($^2 \Pi$) states

It was long ago recognized by Krauss et al. that the anomalously strong SCF binding in MHe($^2 \Pi$) might be caused by the lack of overlap between the diffuse $p\pi$ orbital of M and the occupied $1s$ orbital of He. In contrast, when Ne replaces He, there exists strong overlap between the M($np\pi$) orbital and Ne's $p\pi$ orbitals. The resultant lack of M($p\pi$)-RG($p\pi$) repulsion for He allows a much closer ap-
TABLE IV. Dissociation energies and equilibrium internuclear distances of the states of interest.

<table>
<thead>
<tr>
<th>State</th>
<th>(D_e) (cm(^{-1}))</th>
<th>(R_e) (A)</th>
</tr>
</thead>
</table>
| Li-He(\(^{2}\)\(\Sigma^+\)) | 894\(^b\) | 1.83\(^b\) | 1.78
| Li-Ne(\(^{2}\)\(\Sigma^+\))  | 868\(^c\) | 1.81\(^c\) |
| Li\(^{+}\)-He(\(^{2}\)\(\Sigma^+\)) | 200\(^b\) | 2.47\(^b\) | 2.31
| Li\(^{+}\)-Ne(\(^{2}\)\(\Sigma^+\))  | 214\(^b\) | 2.26\(^b\) |
| Li\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\)) | 546\(^b\) | 1.95\(^b\) | [~1.95]
| Na-He(\(^{2}\)\(\Sigma^+\)) | 601\(^c\) | 1.92\(^c\) |
| Na\(^{+}\)-He(\(^{2}\)\(\Sigma^+\)) | 1001\(^d\) | 2.04\(^d\) | [~2.05]
| Na\(^{+}\)-He(\(^{3}\)\(\Sigma^+\)) | 513\(^b\) | 2.34\(^b\) | [~2.3]
| Na\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\))  | 496\(^d\) | 2.33\(^d\) |
| Na-Ne(\(^{3}\)\(\Sigma^+\)) | 131\(^b\) | 2.83\(^b\) | 2.73
| Na\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\)) | 225\(^b\) | 2.41\(^b\) | [~2.4]
| Na\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\)) | 250\(^d\) | 2.41\(^d\) |
| Na\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\)) | 580\(^d\) | 2.48\(^d\) | [~2.5]
| Na\(^{+}\)-Ne(\(^{3}\)\(\Sigma^+\)) | 508\(^d\) | 2.48\(^d\) |

\(^a\)Taken from Table I. Values in brackets are from one or more estimates which probably have greater uncertainty than the spectroscopically determined values.
\(^b\)This work.
\(^c\)Reference 4.
\(^d\)Reference 69.

Although the overlap argument may rationalize the differences between M-Ne(\(^{2}\)\(\Sigma^+\)) and M-He(\(^{2}\)\(\Sigma^+\)), it does not explain why the Li-He(\(^{2}\)\(\Sigma^+\)) and Na-He(\(^{2}\)\(\Sigma^+\)) excited states are substantially more bound than the cationic Li\(^{+}\)-He and Na\(^{+}\)-He ground states, respectively. Our data (specifically, the difference between the SCF and the correlated-level potentials, see Table V) indicate an additional attraction, due to the \(p\pi\) orbital of M interacting with the RG atom. At the shorter \(R_e\) of MHe(\(^{2}\)\(\Sigma^+\)), this dispersive attractive interaction

is quite substantial: for Ne, with its larger \(R_e\), the same attractive interaction is present but its magnitude is smaller.

To illustrate, the self-consistent field (SCF) interaction potentials for Li\(^{+}\)-He and LiHe(\(^{2}\)\(\Sigma^+\)) are compared in Fig. 5, where they are seen to be much more alike\(^68\) than are the corresponding correlated potentials shown in Fig. 1, consistent with there being an additional attraction present in LiHe(\(^{2}\)\(\Sigma^+\)) compared to Li\(^{+}\)-He. Although the correlation interaction energy involved (~380 cm\(^{-1}\)) might seem at first too large for dispersion-type interactions for an atom like He with such a small polarizability, the Li(\(2p\pi\)) orbital has a very large polarizability and the internuclear distances (~1.8 A) are much smaller than usually encountered for net attractive dispersion-type interactions.

The \(C_6\) coefficient for the \(p\pi\) interaction of Li(\(2p\pi\)) with the He atom has been calculated\(^71\) to be 0.273\times10\(^{-5}\) erg cm\(^6\). For \(R=1.82\) A, this would lead to an attractive energy of ~3800 cm\(^{-1}\), much more than adequate to account for the correlation energy of ~390 cm\(^{-1}\). The profound discrepancy between the \(C_6/R^6\) multipole-approximated dispersive interaction and the \(ab\) initio evaluated correlation energy term has its origin in the “dampening” arising from the interpenetration of the instantaneous multipole densities [i.e., penetration of the Li(\(p\pi\)) and He 1\(s\) orbitals].\(^71\) Due to the unusually short M-He distances, the dampening is expected to be large. A crude estimate of the interpenetration effects can be obtained if we consider the effective center of charge of the “lobes” resulting from the transverse Li(\(2p\pi\)) orbital. A Li(\(2p\pi\))-He distance of only ~2.7 A would be required to produce a dispersive attractive interaction of 390 cm\(^{-1}\), and this would correspond to an effective dispersion “center of charge” of the Li(\(2p\pi\)) orbital (as measured from the Li nucleus in a direction perpendicular to the Li-He bond axis) of ~2.0 A, which is certainly of the right order.

C. More details on the origin of the M\(p\pi\)-Ne repulsion

The qualitative difference between the \(^{2}\Pi\) complexes of He vs Ne manifests itself even at the SCF level, as shown in Table V and Figs. 5 and 6 (analogous data is obtained when Na replaces Li). The SCF interaction energy, \(E_{int}^{SCF}\), is attrac-
electron exchange integrals between pairs of orbitals on A and B. Due to the long-range multipole components for the systems studied, one- and two-electron integrals are combined pieces: the electrostatic interaction energy $E_{inter}$, and a deformation component $E_{def}$.

$E_{def} = E_{int}^{SCF} - E_{int}^{H-L}$.

$E_{int}^{H-L}$ describes the interaction energy as the energy difference between that of the separated fragments ($E_A$ and $E_B$) and the energy for a wave function $\psi_{AB}$ which is an antisymmetrized product of the SCF wave functions of the undeformed $A$ and $B$ fragments: $\psi_{AB} = A^\dagger \psi_A \otimes B^\dagger \psi_B$

$$E_{int}^{H-L} = \frac{\langle \psi_{AB} | H | \psi_{AB} \rangle}{\langle \psi_{AB} | \psi_{AB} \rangle} - E_A - E_B.$$  

The second term of Eq. (1), $E_{int}^{def}$, has its origin in the mutual deformation of the interacting species, and, for the species considered here, is found to be the dominant attractive component of $E_{int}^{SCF}$.

The energy $E_{int}^{H-L}$ is commonly decomposed into three pieces: the electrostatic interaction energy $E_{elst}$, an exchange energy $E_{exch}$, and an orbital orthogonality factor $E_S$

$$E_{int}^{H-L} = E_{elst} + E_{exch} + E_S.$$  

The component $E_{elst}$ gives the classical (Coulomb) interaction between the charge distributions of $A$ and $B$. Due to the spherical symmetry of the RG atoms, $E_{elst}$ does not have any long-range multipole components for the systems studied here. The term $E_{exch}$ is given as a negative sum of two-electron exchange integrals between pairs of orbitals on $A$ and $B$. Hence, $E_{exch}$ is negative (attractive). In the final contribution $E_S$, one- and two-electron integrals are combined with overlap integrals ($S$) between orbitals of $A$ and of $B$ to produce an overall repulsive contribution to $E_{int}^{SCF}$.

The source of additional repulsion in $MNe(21^2)$ can now be clarified. The $np\pi$ orbital of $M$ has zero overlap with the occupied helium valence $1s$ orbital (by symmetry). As a consequence, the contribution from the $np\pi$ orbital to the interfragment overlap $E_S$ term vanishes, but the attractive contribution in $E_{exch}$ remains. However, for noble gases with $s^2p^6$ configurations, the (repulsive) $np\pi$ contribution of $E_S$ no longer vanishes, since the $p\pi$ orbitals of the M and RG atoms have nonzero overlap. One therefore expects more repulsive SCF interaction energies for $MNe(21^2)$ than for $M^+Ne(\Sigma)$, consistent with our findings.

Also consistent with this interpretation are the differences in $\pi$ orbital energies observed for LiHe and LiNe (relative to the $2p$ orbital energy of an isolated excited Li atom) at the respective $R_e$ distances. The singly occupied $\pi$ orbital of LiNe(21$^2$) is destabilized by $\sim$1000 cm$^{-1}$ relative to isolated Li(2p), but for LiHe(21$^2$) the $\pi$ orbital is slightly ($\sim$100 cm$^{-1}$) stabilized. Due to the intervention of the Pauli exclusion principle, the filled $2p\pi$ orbitals of Ne act to repel the higher energy $2p\pi$ orbital of Li(2p).

To further test our hypothesis that the absence of occupied $p\pi$ orbitals is what makes the He atom "special" when interacting with $M(np\pi)$ states, we designed the following numerical experiment. For the noble gases having $s^2p^6$ configurations, the first $M-RG(\Delta^2)$ Rydberg-type states should also have vanishing (repulsive) $E_S$ overlap energies. For such states, the $M nd\delta$ orbital contributes nothing to $E_S$ because it is orthogonal to all RG $s$ and $p$ orbitals. Indeed, the SCF potential energy curve we obtain for Li(3d $2^2$)-Ne(2$\Delta$) has a $D_e$ of 580 cm$^{-1}$ at $\sim$2.2 Å, similar to those for the Li$^+$. Ne cation ground state, where $D_e = 700$ cm$^{-1}$ at 2.2 Å. This is in stark contrast, of course, to the Li(2p $2^2$)-Ne(21$^2$) state, which is $+360$ cm$^{-1}$ repulsive at $R = 2.2$ Å at the SCF level.

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