

$$\ln(P\tau_{\text{ClF-C1F}}) = -5.764 \pm 1.539 + (50.57 \pm 13.26)T^{-1/3}, \quad (3)$$

$$\ln(P\tau_{\text{ClF-Ar}}) = -6.727 \pm 0.772 + (68.44 \pm 6.78)T^{-1/3}, \quad (4)$$

where the  $P\tau$ 's are in  $\mu\text{sec atm}$  and  $T$  ranges from 500 to 1000 K. These expressions are plotted in Fig. 1. Results of studies of vibrational relaxation of  $\text{F}_2$ <sup>2,8</sup> and  $\text{Cl}_2$ <sup>9</sup> are also given in Fig. 1 for comparison.

It is interesting to note that the relative ordering of ClF-Ar and ClF-ClF relaxation times cannot be explained by the Millikan and White<sup>10</sup> (M-W) correlation. The M-W correlation results in a monotonically increasing dependence of  $P\tau$  on the reduced mass for realistic molecular weights and temperatures. Thus the M-W correlation predicts the opposite mass dependence to that observed in this experiment. If one considers a more refined model such as the Landau-Teller or SSH theories<sup>7</sup> the present results imply a substantial difference exists for the effective range parameter for

ClF-Ar as compared to ClF-ClF in order to compensate for the kinetically derived mass effect.

<sup>a)</sup>This work was performed at Boston College in the Department of Physics.

<sup>1</sup>J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.* **44**, 658 (1966)

<sup>2</sup>G. Diebold, R. Santoro, and G. Goldsmith, *J. Chem. Phys.* **60**, 4170 (1974).

<sup>3</sup>G. Diebold and R. Santoro, *Rev. Sci. Instrum.* **45**, 773 (1974).

<sup>4</sup>Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. **37**, (1971).

<sup>5</sup>V. Blackman, *J. Fluid Mech.* **1**, 61 (1956).

<sup>6</sup>T. Cottrell and J. McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths, London, 1961).

<sup>7</sup>J. Clarke and M. McChesney, *The Dynamics of Real Gases* (Butterworths, Washington, D. C., 1964).

<sup>8</sup>G. Diebold, R. Santoro, and G. Goldsmith, *J. Chem. Phys.* **62**, 296 (1975).

<sup>9</sup>W. D. Breshears and P. F. Bird, *J. Chem. Phys.* **51**, 3660 (1969).

<sup>10</sup>R. Millikan and D. White, *J. Chem. Phys.* **39**, 3209 (1963).

## Electronic structure of small metal clusters. II. Anions of $\text{Li}_2$ , $\text{LiNa}$ , and $\text{Na}_2$

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Alkali metal dimers are of considerable experimental and theoretical interest. Most studies of these dimers have focused on the properties of the neutral and their cations. Until quite recently the anions have received little attention. There appear to be no experimental determinations of any of the properties of the alkali dimer anions. However,  $\text{Na}_2^-$ ,  $\text{Na}_3^-$ , and  $\text{Na}_4^-$  have been detected mass spectroscopically.<sup>1</sup> Several theoretical investigations of  $\text{Li}_2^-$  have appeared in the literature, the two most thorough being the configuration-interaction (CI) and equation-of-motion (EOM) calculations of Andersen and Simons<sup>2</sup> and Dixon, Gole, and Jordan,<sup>3</sup> respectively. Bardsley, Junker, and Norcross<sup>4</sup> have carried out pseudopotential calculations of the ground state potential energy curves of  $\text{Na}_2$  and  $\text{Na}_2^-$ .

In the present work the spin-restricted (RHF) and spin-unrestricted (UHF) self-consistent-field (SCF) Hartree-Fock methods<sup>5,6</sup> are employed to investigate the properties of  $\text{Li}_2$ ,  $\text{LiNa}$ , and  $\text{Na}_2$ , and their anions, respectively. For each molecule an initial basis, chosen to provide a good description of the neutral species, was augmented with diffuse  $s$  and  $p$  functions in order to describe the more diffuse charge density of the anion. The exponents of the diffuse functions were varied to optimize the UHF energy of the  $^2\Sigma_u$  ground state of the anion at the equilibrium configuration of the neutral molecule.

The Li basis set was generated from the 6-31G basis of Dill and Pople<sup>7</sup> by uncontracting their three-component  $2s$  function and adding one diffuse  $s$  function and one diffuse  $p$  function. The basis set for Na was formed by adding two diffuse  $s$  and two diffuse  $p$  functions to a  $5s/3p$  contraction of the  $12s/6p$  primitive basis set of Veillard.<sup>8</sup> As an indication of the quality of our basis sets we note that our calculated dipole moment of 0.76 D ( $\text{Li}^b\text{-Na}^{6+}$ ) for  $\text{LiNa}$  is in good agreement with the 0.72 D SCF value of Rosmus and Meyer<sup>9</sup> and the 0.46 D experimental value.<sup>10</sup>

Using the basis sets described above, the ground state anions of  $\text{Li}_2$ ,  $\text{LiNa}$ , and  $\text{Na}_2$  are found to be stable with vertical electron affinities of 0.32, 0.35, and 0.30 eV, respectively, and adiabatic E.A.'s of 0.46, 0.45, and 0.42 eV, respectively. However, it should be noted that basis set inadequacies could cause relative errors as large as 0.06 eV.

The earlier CI<sup>3</sup> and EOM<sup>2</sup> studies on  $\text{Li}_2$  yielded adiabatic E.A.'s of 0.45 and 0.90 eV, respectively. Dixon *et al.*<sup>3</sup> estimated that the true E.A. of  $\text{Li}_2$  is 0.50–0.65 eV. Since the SCF E.A.'s of  $\text{LiNa}$  and  $\text{Na}_2$  are within 0.04 eV of that of  $\text{Li}_2$  and since the electron correlation contribution to the E.A.'s of all three molecules should be nearly the same, we expect that the exact E.A.'s of  $\text{Na}_2$  and  $\text{LiNa}$  should be 0.45–0.65 eV.

The relationship between the dissociation energies (DE) of the anions and neutrals<sup>11</sup> is

$$D_e(AB^-) = D_e(AB) + E.A.(AB) - E.A.(A), \quad (1)$$

where  $E.A.(AB)$  is the adiabatic electron affinity of  $AB$ . Substituting our adiabatic SCF  $E.A.$ 's for the molecules, accurate values<sup>12</sup> for the neutrals' DE's and experimental atomic  $E.A.$ 's in this equation we obtain estimates of 0.88, 0.69, and 0.59 for the DE's of  $Li_2^-$ ,  $LiNa^-$ , and  $Na_2^-$ , respectively. This estimate of the DE for  $Li_2^-$  compares well with the CI<sup>3</sup> value of 0.86 eV. Moreover, if the  $E.A.$  of  $Li_2$  is 0.50–0.65 eV, as was estimated by Dixon *et al.*,<sup>3</sup> then a value of 0.9–1.2 eV would be expected for the DE of  $Li_2^-$ . We therefore conclude that the anion DE's calculated from Eq. (1) are probably as much as 0.3 eV too small and that, for all three molecules, the anion dissociation energies should be within 0.2 eV of the DE's of the neutrals. This is especially interesting since the bond orders of the anions are 1/2 while those of the neutrals are 1.0.

The addition of an electron to the  $2\sigma_u$  orbital causes the  $2\sigma_g$  orbital of  $Li_2^-$  to become more diffuse than that of  $Li_2$  with substantial increases in the contributions from both the diffuse  $s$  and  $p$  basis functions. The  $2\sigma_g$  orbital does not become as diffuse but it does acquire a sizeable contribution from the tightest  $p$  function. The  $2\sigma_u$  orbital of the anion also has a greater contribution from the  $p$  functions than does the neutral. Analogous changes occur for the valence orbitals of  $Na_2$  and  $LiNa$  upon the addition of an "extra" electron.

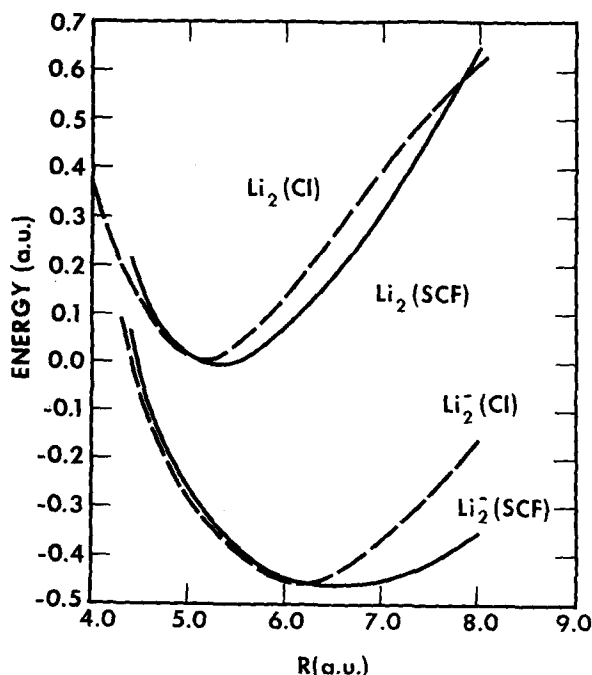


FIG. 1. Potential energy curves of  $X^1\Sigma_g Li_2$  and  $X^2\Sigma_u Li_2^-$ . The solid curves depict the SCF results of the present investigation and the dashed curves are from the CI study of Ref. 3. The potential curves have been shifted so that the minima of both the SCF and CI  $Li_2$  curves are at 0.0 eV.

In Fig. 1 we plot the SCF and CI potential energy curves of  $Li_2$  and  $Li_2^-$ . The SCF curves are from the present investigation while the CI curves are from Ref. 3. The CI calculations yield shorter bond lengths and higher vibrational frequencies. For example, the SCF and CI bond lengths are 5.30 and 5.12 a.u., respectively, while those of  $Li_2^-$  are 6.50 and 6.08 a.u., respectively. The SCF curves of  $Na_2/Na_2^-$  and  $LiNa/LiNa^-$  are very similar in shape to those for  $Li_2/Li_2^-$ , and hence, are not displayed here.

Finally, we note that while the pseudopotential calculations of Ref. 4 yielded a negative value for the vertical  $E.A.$  of  $Na_2$ , the present study indicates that it is positive. We also predict an adiabatic  $E.A.$  in the range of 0.50–0.65 eV which is much larger than the 0.15 eV value obtained in Ref. 4. It is our feeling that the basis set employed in the pseudopotential calculations was not flexible enough to properly describe the  $Na_2^-$  charge density, thus resulting in a qualitatively incorrect  $E.A.$

In summary, our SCF investigations of  $Li_2^-$ ,  $LiNa^-$ , and  $Na_2^-$  result in the prediction of vertically and adiabatically stable anions having (adiabatic)  $E.A.$ 's of 0.46, 0.45, and 0.42 eV, and DE's of 0.88, 0.69, and 0.59, respectively. Electron correlation is expected to cause increases in these values of 0.05–0.20 eV.

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<sup>1</sup>M. Leleyter and P. Joyes, *J. Phys. (Paris)* **35**, L85 (1974).

<sup>2</sup>E. Andersen and J. Simons, *J. Chem. Phys.* **64**, 4548 (1976).

<sup>3</sup>D. A. Dixon, J. L. Gole, and K. D. Jordan, *J. Chem. Phys.* **66**, 567 (1977).

<sup>4</sup>J. N. Bardsley, B. R. Junker, and D. W. Norcross, *Chem. Phys. Lett.* **37**, 502 (1976).

<sup>5</sup>The integral generation utilized the MOLECULE program of J. Amlöf described in Report 74-29 of the University of Stockholm, Institute of Physics.

<sup>6</sup>The SCF calculations were carried out using the GRNFNC program developed by G. Purvis at the University of Florida's Quantum Theory Project.

<sup>7</sup>J. D. Dill and J. A. Pople, *J. Chem. Phys.* **62**, 2922 (1975).

<sup>8</sup>A. Veillard, *Theor. Chim. Acta* **12**, 405 (1968).

<sup>9</sup>P. Rosmus and W. Meyer, *J. Chem. Phys.* **65**, 492 (1976).

<sup>10</sup>J. Graff, P. J. Dagdigian, and L. Wharton, *J. Chem. Phys.* **57**, 710 (1972).

<sup>11</sup>J. P. Lowe, *J. Am. Chem. Soc.* **99**, 5557 (1977).

<sup>12</sup>The dissociation energies used for the neutrals are:  $Li_2$ : 1.03 eV, Ch. Ottinger and R. N. Zare, *J. Chem. Phys.* **51**, 5522 (1969);  $LiNa$ : 0.85 eV, P. J. Bertonecni, G. Das, and A. C. Wahl, *J. Chem. Phys.* **52**, 5112 (1970);  $Na_2$ : 0.74 eV, P. J. Bertonecni and A. C. Wahl (unpublished results), see Ref. 4.