Negative Ion States of Polar Molecules

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Molecular anions play an important role in many chemical reactions. For example, molecular anions are formed in electron attachment in flames^1 and in many reactions occurring in the lower atmosphere.^{2} One of the most important classes of chemical reactions involving anions is bimolecular nucleophilic substitution (S_N2) processes.^{3} Ion cyclotron resonance (ICR) is being used increasingly to determine the equilibrium constants of gas-phase reactions such as

$$AH + B^- = BH + A^-$$

hence allowing the determination of gas-phase acidites.^{4} Negative ion mass spectroscopy^5 has provided much new information on molecules and their anions.

Perhaps the most important property characterizing an anion is its energy relative to that of the neutral molecule. The adiabatic electron affinity of a molecule is refined as $EA_{Ad}(M) = E_{tot}[M(R_e{}^M)] - E_{tot}[M^-(R_e{}^{M^-})]$ and the corresponding vertical value as $EA_{vert}(M) = E_{tot}[M(R_e{}^M)] - E_{tot}[M^-(R_e{}^M)]$. In these expressions $E_{tot}[M]$ and $E_{tot}[M^-]$ are the total energies of the neutral and anion, respectively, and $R_e{}^M$ and $R_e{}^{M^-}$ refer to the equilibrium coordinates of the neutral molecule and anion, respectively.

If EA_{Ad} is negative, then the anion is unstable with respect to autodetachment of the electron. This is the situation for the gas-phase anions of many molecules such as ethylene, formaldehyde, and benzene.^{6} Recent years have witnessed the application of a wide variety of experimental techniques to the determination of accurate electron affinities. In particular, photodetachment spectroscopy, ICR, charge-transfer processes, and the magnetron method have provided a wealth of data on stable anions, while electron scattering techniques such as electron transmission spectroscopy, the trapped electron method, and the SF_6 scavenger method have provided information on temporary anions with lifetimes as short as 10^{-15} s.

In this Account we focus attention on the anions of highly polar molecules. This class of anions has attracted considerable interest.$^{7-29}$ Experimentally this interest has been stimulated by photodetachment studies of $LiCl^-$ by Carlsten, Peterson, and Lineberger^{13} and by the discovery of large cross sections for the vibrational excitation^8 via electron impact on HF, H_2O, HCl, and HBr.

Much of the theoretical interest in the anions of polar molecules is due to the special properties of "dipole-dominated" anions. Within the Born–Oppenheimer approximation, i.e., the assumption that one can separate the electronic and nuclear degrees of freedom and solve for the electronic energy for an arrangement of

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(1) R. S. Gould and W. J. Miller, *J. Chem. Phys.*, **62**, 644 (1975).

(2) F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **61**, 3181 (1974).

(3) W. N. Olmstead and J. I. Brauman, *J. Am. Chem. Soc.*, **99**, 4219 (1977); J. D. Payzant, K. Tanaka, L. D. Betowski, and D. K. Bohme, *ibid.*, **98**, 894 (1976).

(4) R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, **95**, 8462 (1973); B. S. Freiser and J. L. Beauchamp, *ibid.*, **99**, 3214 (1977).

(5) J. G. Dillard, *Chem. Rev.*, **73**, 589 (1973).

(6) K. D. Jordan and P. D. Burrow, *Acc. Chem. Res.*, **11**, 341 (1978).

(7) R. F. Wallis, R. Herman, and H. W. Milnes, *J. Mol. Spectrosc.*, **4**, 51 (1960).

(8) O. H. Crawford, *Proc. Phys. Soc., London*, **91**, 279 (1967); C. A. Coulson and M. Walmsley, *ibid.*, **91**, 31 (1967); W. B. Brown and R. E. Roberts, *J. Chem. Phys.*, **46**, 2006 (1967); J. M. Levy-Leblond, *Phys. Rev.*, **153**, 1 (1967); M. H. Mittleman and V. P. Myerscough, *Phys. Lett.*, **23**, 545 (1966); J. E. Turner, V. E. Anderson, and K. Fox, *Phys. Rev.*, **174**, 81 (1968).

(9) W. R. Garrett, *Phys. Rev. A*, **3**, 961 (1971); *Mol. Phys.*, **24**, 465 (1972).

(10) O. H. Crawford, *Mol. Phys.*, **20**, 585 (1971); see also L. D. Landau and E. M. Lifshitz, "Quantum Mechanics", 2nd ed., Pergamon Press, Oxford, 1959, pp 118–121.

(11) O. H. Crawford and W. R. Garrett, *J. Chem. Phys.*, **66**, 4968 (1977).

(12) O. H. Crawford and B. J. D. Koch, *J. Chem. Phys.*, **60**, 11 (1974).

(13) J. L. Carlsten, J. R. Peterson, and W. C. Lineberger, *Chem. Phys. Lett.*, **37**, 5 (1976).

(14) S. E. Novick, T. J. Mulloney, and W. C. Lineberger, unpublished results.

(15) R. C. Slater, M. G. Fickes, W. G. Becker, and R. C. Stern, *J. Chem. Phys.*, **60**, 4692 (1974); **61**, 2290 (1974); W. G. Becker, M. G. Fickes, R. C. Slater, and R. C. Stern, *ibid.*, **61**, 2283 (1974).

(16) (a) M. R. H. Rudge, S. Trajmar, and W. Williams, *Phys. Rev. A*, **13**, 2074 (1976); (b) F. T. Smith, D. L. Huestis, D. Mukherjee, and W. H. Miller, *Phys. Rev. Lett.*, **35**, 1073 (1975); (c) K. Takayanagi and Y. I. Itikawa, *Adv. Atomic Mol. Phys.*, **6**, 105 (1970); (d) F. A. Gianturco and N. K. Rahman, *Chem. Phys. Lett.*, **48**, 300 (1977); (e) L. A. Collins and D. W. Norcross, *Phys. Rev. Lett.*, **38**, 1208 (1977); (f) D. W. Norcross, private communication.

(17) L. Dube and A. Herzenberg, *Phys. Rev. Lett.*, **38**, 820 (1977).

(18) G. Seng and F. Linder, *J. Phys. B*, **9**, 2538 (1976); K. Rohr and F. Linder, *ibid.*, **9**, 2521 (1976); K. Rohr, preprint.

(19) (a) K. M. Griffing, J. Kenney, J. Simons, and K. D. Jordan, *J. Chem. Phys.*, **63**, 4073 (1975); (b) K. D. Jordan and W. Luken, *ibid.*, **64**, 2760 (1976); (c) K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Andersen, and J. Simons, *J. Chem. Phys.*, **64**, 4370 (1976).

(20) (a) K. D. Jordan, *J. Chem. Phys.*, **65**, 1214 (1976); (b) *ibid.*, **66**, 3305 (1977); (c) K. D. Jordan and J. J. Wendoloski, *Mol. Phys.*, **35**, 223 (1978).

(21) K. D. Jordan and J. J. Wendoloski, *Chem. Phys.*, **21**, 145 (1977).

(22) K. D. Jordan and R. Seeger, *Chem. Phys. Lett.*, **54**, 320 (1978).

(23) J. A. Stockdale, F. J. Davis, R. N. Compton, and C. E. Klots, *J. Chem. Phys.*, **60**, 4279 (1974); R. N. Compton, P. W. Reinhardt, and C. D. Cooper, preprint.

(24) D. A. Armstrong and S. S. Nagu, *J. Phys. Chem.*, **79**, 2875 (1975).

(25) We have found that the orbital relaxation and electron correlation contributions to the EA of LiH are 0.03 and 0.07 eV, respectively. In a recent SCF CI study of LiH and LiH^- it was found that the electron correlation contribution to the EA is 0.06 eV: B. Liu, K. O. Ohata, and K. Kirby-Docken, *J. Chem. Phys.*, **67**, 1850 (1977). Moreover, CI calculations of the EA of LiCl show that the contribution due to electron correlation is <0.1 eV: B. Liu, personal communication.

(26) (a) K. D. Jordan, *Chem. Phys. Lett.*, **40**, 441 (1976); (b) G. Purvis and K. D. Jordan, unpublished results.

(27) P. D. Burrow, *J. Phys. B*, **7**, 385 (1975).

(28) J. P. Ziesel, I. Nenner, and G. J. Schulz, *J. Chem. Phys.*, **63**, 1943 (1975).

0001-4842/79/0112-0036$01.00/0

fixed nuclei, one finds the intriguing result that any molecule with a dipole moment greater than 1.625 D must possess an infinite progression of bound anions. This follows from the unique properties of electron–dipole systems and from the fact that one can always surround a neutral molecule with a hard sphere of sufficient radius that only the dipole field is important outside of the sphere. The existence of the critical moment follows from the observation that the fixed-finite dipole model[7-12] (hereafter referred to simply as the dipole model) of an electron in the field of two fixed point charges, $+q$ and $-q$, separated by a distance R, has an infinite number of bound σ states for dipole moments, $\mu = qR$, greater than 1.625 D and no bound states for dipole moments less than this. Moreover, the same critical moment exists for a point dipole surrounded by any spherically symmetric repulsive core dropping off faster than the square of the inverse of the electron–molecule separation.

The results are drastically altered when one considers corrections to the Born–Oppenheimer approximation.[9-11] Crawford and Garrett[11] have shown that if the Born–Oppenheimer electron affinity is as large as one-tenth to one-twentieth the molecular rotational constants, then the anion will remain bound when the nonstationary aspect of the problem is treated. The critical moments of a nonstationary dipole depend separately on q and R as well as on the moment of inertia and the rotational state. Even in the limit of zero temperature, the critical moments of the nonstationary dipole are 10–30% greater than 1.625 D. Moreover, only a finite number of bound anion states persist. The corrections to the Born–Oppenheimer approximation are especially important for those molecules with dipole moments only slightly in excess of 1.625 D (in which case the Born–Oppenheimer electron affinities are very small). Even when the Born–Oppenheimer approximation is valid, the applicability of the dipole model for the calculation of anion properties is now known to be questionable. The major deficiency of the dipole model appears to be the neglect of the core electrons on the electropositive atom.

Our major emphasis here is on the dipole-dominated anions of molecules with dipole moments considerably greater than 1.625 D. We remind the reader that there are many molecules with dipole moments less than 1.625 D that have stable anions, e.g., O_2 and NO_2. There is much interest in the role of the dipole field in determining the properties of anions. One property which is of considerable interest is the threshold behavior of the photodetachment cross section of the anion as a function of the dipole moment of the neutral molecule.

There is also considerable interest in the vibrational excitation cross sections of molecules[17,18,27-29] such as H_2O, HF, HCl, and HBr upon electron impact. These molecules are not expected to have bound dipole-dominated anions since the dipole moments of HCl and HBr are less than the critical moment, while those of HF and H_2O, although greater than the critical moment, are sufficiently small that their Born–Oppenheimer EA's are much smaller than the rotational constants. However, all four of these molecules display very large vibrational excitation cross sections, suggesting that temporary anion states are involved.[18] Since the angular distribution of the scattered electrons at low energy is predominantly s wave,[18] ruling out shape resonances, it has been suggested[17-18] that virtual negative ion states with energies slightly above those of the neutrals are responsible for the large cross sections.

Ionic Molecules

Ground State Anions. In the photodetachment studies of $LiCl^-$ by Carlsten et al.[13] the anion was prepared by means of a discharge, separated from the other products mass spectroscopically, and its photoelectron spectrum determined. With the assumption that they had detected the first vibrational level of $LiCl^-$, Carlsten et al. deduced an electron affinity (EA) of 0.61 ± 0.02 eV for LiCl. Since some $LiCl^-$ was vibrationally excited, it was also possible to obtain a value of 0.065 ± 0.010 eV for $\hbar\omega_e$ of the anion, close to the value of 0.080 eV for the parent neutral. Carlsten et al. also observed that for a dipole moment of the size of that of LiCl (7.13 D) and with the reasonable choice $q = 1$ the dipole model yields an EA of about 4.8 eV, eight times larger than the value determined experimentally.

This large discrepancy prompted us to initiate ab initio LCAO–MO–SCF studies of $LiCl^-$ and the anions of other polar molecules. We refer to these as Hartree–Fock calculations even though more flexible basis sets would actually be needed to attain convergence to Hartree–Fock limits. The most important consideration in the calculation of the properties of dipole-dominated anions is the use of basis sets capable of (a) accurately describing the dipole field of the neutral molecule and (b) containing sufficiently diffuse functions to permit the "extra" electron to attach in the dipole field hybridized away from the electronegative end of the molecule.[19,20,30] For ionic molecules, such as the alkali halides, near Hartree–Fock wavefunctions yield dipole moments correct to about 0.2 D. The values of the orbital exponents of the diffuse functions are determined by either maximizing $-\epsilon_{LUMO}$, the negative of the orbital energy of the lowest unoccupied molecular orbital (LUMO) of the neutral molecule, or by minimizing the Hartree–Fock energy of the anion.

The Koopmans' theorem approximation, EA(KT) = $-\epsilon_{LUMO}$, gives the binding energy of an electron assuming that there is no readjustment of the charge density of the neutral molecule upon the addition of the extra electron. The procedure of determining the exponents of the diffuse functions by maximizing $-\epsilon_{LUMO}$ is justified only if ϵ_{LUMO} is negative. This is the case for any molecule with a dipole moment greater than 1.625 D provided that a sufficiently flexible basis set is employed. This procedure is most useful when the orbital relaxation and correlation corrections to the $-\epsilon_{LUMO}$ estimate of the EA are small and if the energy of the neutral molecule does not vary appreciably with the exponents of the diffuse functions. These conditions will be satisfied when the LUMO is localized in a region of space where the charge density, due to the occupied orbitals, is small. This is precisely the situation which

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(29) H. S. Taylor, E. Goldstein, and G. A. Segal, *J. Phys. B*, **10**, 2253 (1977); E. Goldstein, G. A. Segal, and R. W. Wetmore, *J. Chem. Phys.*, **68**, 271 (1978).

(30) We have found that the 6-31G split-valence shell Gaussian basis sets of Pople and co-workers provide good starting basis sets; see J. D. Dill and J. A. Pople, *J. Chem. Phys.*, **62**, 2922 (1975); and references therein.

Table I
Dipole Moments (D) and Calculated Vertical Electron Affinities (eV)

	dipole moment		EA				
species	calcd	exptl[a] (or prev calcd)	$-\epsilon_{LUMO}$	ΔSCF	with correlation	estd[h]	ref[e]
LiH	6.00	5.88	0.20	0.23	0.30	0.31	19c, 20c, 25
LiF	6.53	6.33	0.30	0.31	g	0.38	19c, 22
LiCl	7.58	7.17	0.48	0.54	(0.61 ± 0.02, exptl)	0.60	19b
LiN	7.20	6.17[b]	0.36	--	--	0.40	20a
LiOH	4.58	4.87[b]	0.13	0.15	--	0.22	20a
LiCN	9.44	9.66[b]	0.59	0.65	--	0.74	20a
LiNC	8.55	8.90[b]	0.49	--	--	0.62	20a
NaH	7.11	6.73[c]	0.26	0.28	0.36[f]	0.33	20c, 20a, 19c
NaF	8.19	8.15	0.41	0.42	--	0.48	22
NaCl	9.42	9.00	0.57	0.61	--	0.67	20c
KH	7.75	--	0.26	0.28	--	0.34	26b
BeO	7.12	7.1 ± 0.3[d]	1.75	2.10	g	2.30	22, 19c
MgO	8.46	8.7 ± 0.5[d]	1.31	2.64	--	3.00	22
HF	2.29	1.82	$\sim 10^{-5}$	--	--	<0	21
H_2O	2.32	1.85	$\sim 10^{-5}$	--	--	<0	21
HCN	3.24	2.98	$\sim 10^{-3}$	--	--	0.0004	21
CH_3CN	4.01	3.92	$\sim 10^{-4}$	--	--	0.0005	21

[a] R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., NSRDS-NBS10, 1967. [b] H. F. Schaefer, "Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, Mass., 1972. [c] E. S. Sachs, J. Hinze, and N. H. Sabelli, *J. Chem. Phys.*, **62**, 3367 (1975). [d] M. Yoshimine, *J. Phys. Soc. Jpn.*, **25**, 1100 (1968). [e] The results listed in the table correspond to the first reference. [f] The value of the correlated EA for NaH is from ref 19c. [g] Correlated EA's of BeO and LiF were presented in ref 19c. However, the basis sets utilized in that study were not as flexible as those used in ref 22. Thus these values have not been included in the table. [h] These values have been determined by adding to the ΔSCF EA's estimates of the electron correlation contributions. An attempt has also been made to correct for the errors introduced into the EA's due to those in the dipole moments. In the case of HF and H_2O, the corrections to the Born–Oppenheimer approximation will cause the weakly bound dipole-dominated anions to be pushed into the continuum.

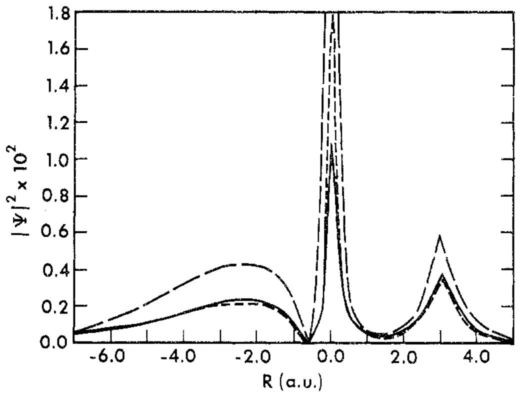

Figure 1. Charge distribution of the LUMO of LiH along the internuclear axis for three different basis sets. The Li and H atoms are located at R = 0.0 and 3.0 au, respectively. The long dashes give the results obtained from the 6-31G basis; the short dashes denote the results of calculations using the 6-31G basis set supplemented with a 1s GTO (exponent 0.009, located at −5.7 au); and the solid line gives the results obtained from the 6-31G basis set supplemented with diffuse 2s and 2p functions on the Li atom. The LUMO is unbound in the 6-31G basis set and bound by 0.20 eV in the augmented basis sets. Reproduced with permission from ref 20c. Copyright 1978 Taylor & Francis, Ltd.

one encounters for the LiX and NaX molecules. As an illustrative example, the LUMO of LiH is shown in Figure 1. Over 90% of the charge density is to the left of the nodal surface passing through R = −0.6 au.

As further substantiation of the above procedure, we note that the Koopmans' theorem, ΔHF [E_{HF}(neutral) − E_{HF}(anion)], and experimental EA's of LiCl are 0.48, 0.54, and 0.61 ± 0.02 eV, respectively. Relaxation of the frozen core approximation inherent in the Koopmans' theorem treatment (i.e., allowing the originally occupied orbitals to readjust due to the presence of the extra electron) results in an increase in the EA of only 0.06 eV. The difference between the experimental and ΔHF EA's is also 0.06 eV; presumably this is associated largely with the difference in the correlation energies of the neutral and the anion.[25] The potential energy curves for LiCl and $LiCl^-$ are presented in Figure 2.

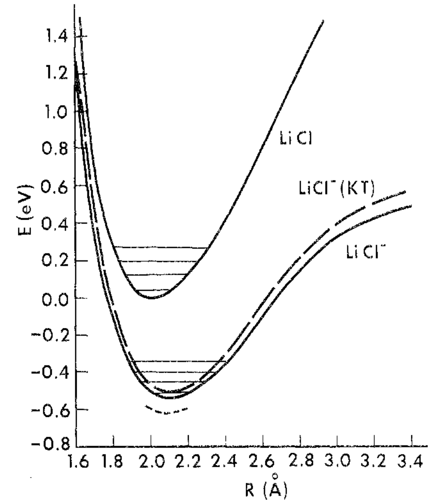

Figure 2. LiCl and $LiCl^-$ potential curves. The LiCl curve is constructed from experimental data. The $LiCl^-$ curve is obtained by subtracting at various internuclear separations the ΔHF EA's from the experimental LiCl potential curve. The long-dashed curve, labeled KT, is obtained by adding at various internuclear separations the energy of the 7σ orbital to the experimental LiCl curve. The positions of the first four vibrational levels of LiCl and $LiCl^-$ are indicated by horizontal lines. The short-dashed curve represents schematically the experimental data for the $LiCl^-$ ground state (Carlsten et al., 1976). Reproduced with permission from ref 19b. Copyright 1976 American Institute of Physics.

One of the most interesting findings of the theoretical studies is that nearly linear relationships exist between the electron affinities and the dipole moments for both

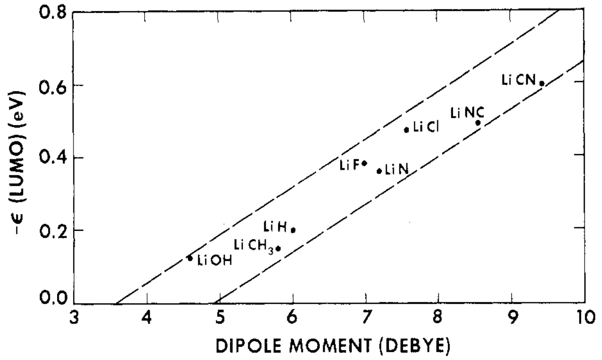

Figure 3. Koopmans' theorem estimate of the electron affinity, $-\epsilon$(LUMO), vs. calculated dipole moment. The dots represent the results of calculations at the equilibrium geometries of various LiX compounds. The two dashed lines provide bounds to the results obtained from limited calculations for nonequilibrium structures. Reproduced with permission from ref 20a. Copyright 1976 American Institute of Physics.

the LiX and NaX molecules. To a good approximation, for LiX molecules

$$\epsilon_{\mathrm{LUMO}} = 0.56 - 0.129\mu$$

and for NaX molecules

$$\epsilon_{\mathrm{LUMO}} = 0.50 - 0.123\mu$$

In these expressions energy is in electronvolts and μ in debyes. The results for the LiX compounds are presented in Figure 3. These relationships are useful for dipole moments between 5 and 10 D but are qualitatively incorrect for smaller dipole moments. Were increasingly diffuse functions added to the basis sets, then ϵ_{LUMO} would asymptotically approach zero energy as the dipole moment approaches 1.625 D.[20b] Upon comparison of these two relationships, one concludes that given LiX and NaX molecules having the same dipole moment, then the EA of the lithium compound will be somewhat greater. This is consistent with observation that the ionization potential of Li is greater than that of Na.

Since the corrections to the KT EA's of the MX compounds (M = alkali; X = halogen, OH, CN, etc.) are relatively small, the exact EA's should also depend nearly linearly on μ. Also, since the dipole moments vary nearly linearly with the M–X bond length over a wide range of internuclear separations, the various estimates of the EA's depend approximately linearly on R.

Our studies[22] of BeO and MgO, isoelectronic with LiF and NaF, respectively, indicate that the alkaline earth oxides are fundamentally different from the alkali halides. One difference, which has also been noted by Yoshimine,[31] is that the dipole moment functions of the alkaline earth oxides display maxima at bond lengths, R_m, near their equilibrium bond lengths, R_e. As shown in Figure 4 for MgO, $-\epsilon_{\mathrm{LUMO}}$ still closely "tracks" the dipole moment curve. However, while $-\epsilon_{\mathrm{LUMO}}$ decreases for bond lengths greater than R_m, the ΔHF EA and the true EA continue to increase.

The neglect of orbital relaxation (and probably also electron correlation) corrections to the EA is a much poorer approximation for BeO and MgO than for the alkali halides. The charge of an alkali atom in an alkali halide is essentially +1 while the Mg of MgO, and to a lesser extent the Be of BeO, are dipositive. Consequently, the LUMO's of MgO and BeO are less delocalized than those of the alkali compounds, thereby resulting in increased contributions of orbital relaxation and correlation to the EA. The calculated ΔHF EA's corresponding to the formation of the ground state anions of BeO and MgO are 2.1 and 2.6 eV, respectively; the correlated values should be somewhat larger.

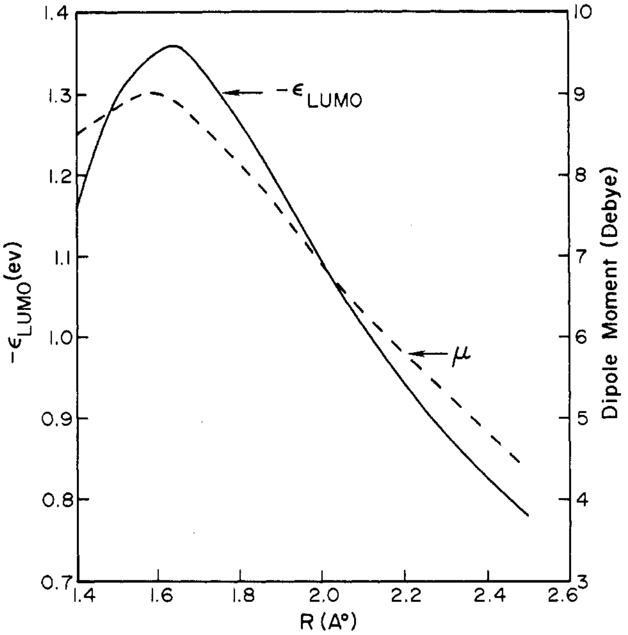

Figure 4. Dipole moment and Koopmans' theorem electron affinity of MgO as functions of internuclear separation. Reproduced with permission from ref 22. Copyright 1978 North-Holland Publishing Co.

The much larger EA's of BeO and MgO compared to those of the alkali halides can be qualitatively understood within the framework of the dipole model. In particular, we note that in the dipole model the following relationship holds for two dipoles with the same dipole moment but with different bond lengths and charges:

$$\mathrm{EA}_1/\mathrm{EA}_2 = q_1^2/q_2^2 = R_2^2/R_1^2$$

For example, using the bond lengths of LiCl and BeO, which have nearly the same dipole moment, one obtains R^2(LiCl)/R^2(BeO) = 2.5, while using the ΔHF EA's one finds EA(BeO)/EA(LiCl) = 3.9.

Excited-State Anions. We have investigated the first excited dipole-dominated $^2\Sigma$ anions for several molecules with $^1\Sigma$ ground states and in all cases have found a very small binding energy in the Born–Oppenheimer approximation. For LiCl the second $^2\Sigma$ anion state was found to be bound by only 0.007 eV. The binding energy of the second $^2\Sigma$ anion of the other alkali halides and alkali hydrides is of the same order of magnitude. Although very small, these binding energies are still greater than the molecular rotational constants, and hence, according to the criterion of Crawford and Garrett, the ions should remain bound at low temperatures even when the nonstationary aspect of the problem is treated. The second $^2\Sigma$ states of the BeO and MgO anions are more strongly bound than those of the alkali halides.[22] The $X^2\Sigma \rightarrow A^2\Sigma$ transition of MgO$^-$ and BeO$^-$ should be particularly amenable to spectroscopic study.

There is also considerable interest in low-lying $^2\Sigma$ and $^2\Pi$ temporary (i.e., resonance) anion states of the alkali

(31) M. Yoshimine, *J. Phys. Soc. Jpn.*, **25**, 1100 (1968).

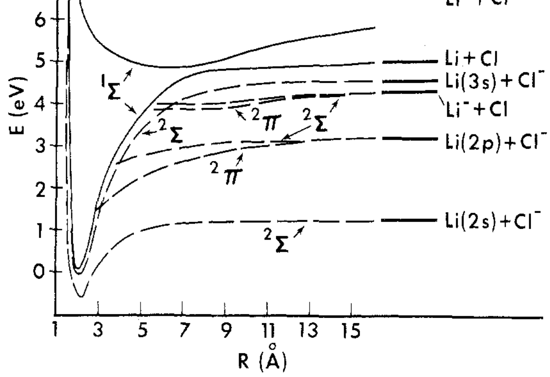

Figure 5. Schematic potential curves of LiCl and $LiCl^-$. The solid lines represent the $X^1\Sigma$ and $A^1\Sigma^+$ potential curves of LiCl which display an avoided crossing near 8 Å. The dashed lines represent the $LiCl^-$ potential curves. The large *R* portions of these curves were constructed from consideration of the asymptotic interactions. Near R_e, the lowest two $^2\Sigma$ anion curves are obtained from the ab initio calculations. Avoided crossings between the anion curves have been neglected.

halides correlating to the ^2P M + ^1S X^- dissociation limits. The potential energy curves of these and several other states of $LiCl^-$ and LiCl are reproduced in Figure 5. These curves are the same as those presented in ref 19b except that the $^2\Pi$ curve has been drawn as attractive, to correspond to the results of SCF calculations by Stevens[32,33] for the corresponding curve of LiF^-.

Electron–LiF scattering calculations of Collins and Norcross[16e] have indicated that LiF should have σ and π shape resonances (i.e., autodetaching anions) at energies close to those calculated by Stevens for the excited Σ and Π states. Quite surprisingly, scattering calculations on LiCl failed to reveal structure due to these resonances. Novick et al.[14] have carried out photoabsorption studies on $NaCl^-$, $NaBr^-$, and NaI^- which seem to indicate excitation of the anions from their ground states into resonance states near 2.1 eV. Whether the $^2\Sigma$ or $^2\Pi$ resonance states mentioned above are playing a role in the photoabsorption is unclear.

Not all anion states of highly polar molecules are of the dipole-dominated variety. For example, the addition of an electron to the low-lying π^* orbital of CH_3NO_2 (μ = 3.46 D) gives rise to a stable anion bound by ~0.5 eV.[23] CH_3NO_2 will also have a stable dipole-dominated $^2\Sigma$ anion provided its Born–Oppenheimer EA is sufficiently large. In such a case, the dipole-dominated $^2\Sigma$ anion would be an excited state and could perhaps be observed spectroscopically via optical absorption from the $^2\Pi$ ground state.

Highly Polar Nonionic Molecules

Many nonionic polar molecules have dipole moments[34] greater than 1.625 D; for example, HF (1.82 D), H_2O (1.85 D), H_2CO (2.2 D), HCN (2.98 D), CH_3NO_2 (3.46 D), CH_3CN (3.92 D), $C_6H_5NO_2$ (4.22 D), and $(HF)_2$ (2.99 D). These molecules are expected to have substantially smaller EA's than do ionic species with comparable dipole moments.

The relative error in the EA for a given error in the dipole moment increases rapidly as the dipole moment approaches the critical moment from above. While a 0.2–0.4 D error in the dipole moment might give rise to an error of 5–15% in the calculated EA of an alkali halide, it can introduce orders-of-magnitude errors into the EA's of HF, H_2O, H_2CO, and HCN. In a single determinantal approach one can usually calculate dipole moments correct to about 0.2 D provided a good basis set (at least atomic double-zeta plus polarization functions or double-zeta[35] reoptimized for the molecular environment) is employed. However, to calculate dipole moments much more accurately than this is a formidable task requiring large basis sets as well as extended configuration interaction. For example, SCF calculations[21] on HF and H_2O employing large s/p basis sets yielded dipole moments about 0.4 D larger than the experimental values. As a result, the calculated Born–Oppenheimer EA's of 10^{-5} eV may be too large by a factor of 100–1000. In any case, since the H_2O and HF EA's are much smaller than the respective rotational constants, the anions are not expected to be stable. The connection between the weakly bound Born–Oppenheimer states of the anion and the virtual states, believed to be responsible for the large vibrational excitation cross sections at threshold for electron impact,[17,18,29] is not well understood.

Molecules with Born–Oppenheimer EA's within a factor of 10–20 of their rotational constants are particularly interesting since, given sufficiently accurate Born–Oppenheimer wavefunctions, one might then treat perturbatively the nonstationary aspect of the problem. Perhaps the simplest molecule with a Born–Oppenheimer EA of the same order of magnitude as its rotational constant is HCN. SCF calculations[21] using a large s/p basis set gave an EA for HCN which is a factor of four larger than the rotational constant.[21] However, the calculated dipole moment was 0.26 D larger than the experimental value, and it was estimated that as a result the EA could be too large by a factor of 2–3. In order to obtain a description of the anion sufficiently accurate to be utilized in a study of the corrections to the Born–Oppenheimer approximation, it would probably be necessary to reduce the error in the calculated dipole moment to less than 0.1 D. This would require a very expensive calculation.

CH_3CN^- is of particular interest since Compton and co-workers[23] have found that collisions of Rydberg atoms (for example, excited Ar atoms) with CH_3CN give rise to stable CH_3CN^- with a cross section of approximately 10^{-12} cm^2. On the other hand, alkali atom collisions with CH_3CN did not yield the stable anion. Apparently, the cross section is large for the transfer of an electron from a loosely bound Rydberg orbital to the very diffuse dipole-dominated σ-type orbital of CH_3CN, while it is small for the transfer of an electron from the relatively tight outer s electron of an alkali

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(32) W. Stevens, unpublished results.

(33) In the resonance region the SCF calculations on the $^2\Sigma$ and $^2\Pi$ states are not variational. In fact, if sufficiently diffuse functions were added to the basis set, the calculations would "collapse" to LiF plus a free electron.

(34) The $(HF)_2$ dipole moment is from T. R. Dyke, B. J. Dyke, and W. Klemperer, *J. Chem. Phys.*, 56, 2442 (1972). The other experimental dipole moments quoted in this article are from R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", National Standard Reference Data Series, National Bureau of Standards, Washington, D.C., NSRDS-NBS10, 1967.

(35) Double zeta, in the sense that we use the term, includes, for example, 2p and 2p′ functions on Li and Be. In this regard, we are referring to basis sets similar to the 6-31G basis sets of Pople and co-workers (see ref 30).

atom. The experimental determination of the cross sections of the processes

$$\mathrm{Na}(n,l) + \mathrm{CH_3CN} \rightarrow \mathrm{Na^+} + \mathrm{CH_3CN^-}$$

as functions of the quantum numbers n and l should allow the determination of the EA of CH_3CN.

Ab initio calculations[21] on CH_3CN gave an EA of 1×10^{-4} eV which is 2.5 times larger than the rotational constant. The calculated dipole moment was 4.01 D, in good agreement with the experimental value of 3.92 D. The dipole moment of CH_3CN is sufficiently large that an error of 0.09 D in its value should not result in an appreciable error in the EA. However, the good agreement between the calculated and experimental dipole moments is probably fortuitous since the calculations assumed 109.5° angles around the central carbon. Furthermore, due to convergence problems, the basis set used for CH_3CN was not as flexible as that for HCN. It is likely that the actual EA may be as large as 5×10^{-4} eV.

Both ab initio calculations and experimental studies suggest that the ground-state anion of an isolated CH_3CN molecule is a dipole-dominated species, contrary to the predictions of simple MO pictures. The question concerning the structure of the CH_3CN^- ion in the condensed phase is particularly interesting. On the one hand, most ions tend to be appreciably stabilized in glasses and crystals. On the other hand, we would expect that, like Rydberg states, the dipole-dominated anions, on account of their very diffuse wave functions, would be destabilized in the condensed phases. Takeda, Williams, and co-workers[36] have determined the ESR spectrum of CH_3CN^- in matrices and crystals. They have suggested that the CCN angle of the anion is about 130°. Since an electron trapped in the dipole field of an isolated CH_3CN is not likely to cause a bending of the CCN bond, we believe that the CH_3CN^- ion observed in condensed phase probably does not correlate with the dipole-dominated gas phase species.

Electron Attachment to Excited States

So far we have restricted our discussion to anions formed by electron attachment to highly polar ground-state anions. An electron may also attach in the dipole field of a highly polar excited state of a molecule to yield an anion which is stable with respect to its parent state but which autoionizes to the lower lying states of the neutral. For example, while the inert-gas halides have rather nonpolar, van der Waals ground states, they possess low-lying ionic excited states (with dipole moments of the order of 9 D) in which an electron has been promoted from the inert gas atom to the halogen. Calculations[37] indicate that there are dipole-dominated anions lying below the ionic parent states. Similarly, many organic molecules have highly polar excited states arising from intramolecular charge transfer. These should also possess dipole-dominated anion states in the gas phase.

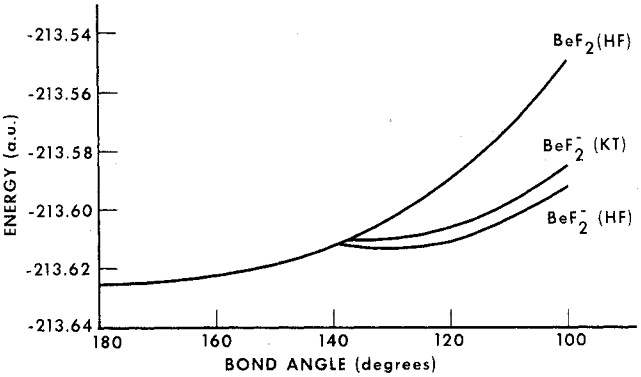

Figure 6. Bending potential energy curves of BeF_2 and BeF_2^-. The BeF_2 results are from Hartree–Fock calculations, while both Koopmans' theorem and Hartree–Fock results are reported for the anion.

Conclusions

In this Account we have dealt primarily with the properties of dipole-dominated anions. At the present time, very little is known about the nature of chemical reactions involving this class of anions. One particularly interesting class of reactions about which data are becoming available is that involving charge transfer between Rydberg atoms and polar molecules. The charge-transfer reaction between an alkali anion and an alkali halide, for example

$$\mathrm{Na^-} + \mathrm{LiCl} \rightarrow \mathrm{LiCl^-} + \mathrm{Na}$$

would be especially interesting since it involves a nearly resonant charge transfer.

To date, most theoretical studies on the anions of polar molecules have dealt with molecules with one electropositive and one electronegative group. We have recently begun to extend our studies to more complicated species with two or more electropositive and/or electronegative groups. Of particular interest is the question of whether an electron can attach in a quadrupole field. For example, the dimers of the alkali halides and alkali hydrides in their rhombic equilibrium configurations have large quadrupole but zero dipole moments. SCF calculations[26a] indicate that the rhombic form of $(LiH)_2$ does not attach an electron to form a stable anion but that the electron affinity of linear LiHLiH species is sufficiently large that it more than compensates for the energy required to distort the cyclic form of the molecule to the linear structure. Ebinghaus[38] has used electron impact on alkali halide dimers to produce anions of the monomers. Presumably the electron is captured into a resonance state of the dimer, and the monomer anion is then formed in a dissociative attachment process.

The anions of the alkaline earth dihalides and the dialkali oxides are of special interest. The equilibrium structures of BeF_2, MgF_2, and Li_2O, for example, are known to be linear and therefore possess zero dipole moments. However, their dipole moments increase rapidly with decreasing bond angle. This suggests the possibility of stable or metastable dipole-dominated anions. The results of recent calculations[39] on BeF_2 and its anion are presented in Figure 6. The anion is found

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(36) K. Takeda and F. Williams, *Mol. Phys.*, 17, 677 (1969); M. A. Bonin, K. Takeda, K. Tsuji, and F. Williams, *Chem. Phys. Lett.*, 2, 363 (1968); M. A. Bonin, Y. J. Chang, E. D. Sparague, K. Takeda, J. T. Wang, and F. Williams, in "Nobel Symposium" Vol. 22, Per-Olof Kinell, Bengt Ranby, and Vera Runnstrom-Reis, Eds., Wiley, 1973, p 103.

(37) N. Winters, abstract of paper contributed to the Ohio State Spectroscopy Symposium, 1977; personal communication.

(38) H. Von Ebinghaus, *Z. Naturforsch.*, 199, 727 (1964).

(39) B. Seiders, W. L. Luken, R. B. Blickensderfer, and K. D. Jordan, unpublished results.

to be stable relative to the neutral molecule for bond angles less than about 140°. Moreover, it possesses a shallow minimum near 135°. The lifetime of the anion will depend on the Franck–Condon overlap of its vibrational wavefunctions with those of the neutral molecule. The situation is similar to that for the CO_2^- anion.[40] The lifetime of this anion is sufficiently long that it can be observed mass spectroscopically. We have also found[39] that bent MgF_2^- is stable by 0.5 eV. The greater stability of MgF_2^- compared to BeF_2^- can be largely ascribed to the smaller bending force constant of MgF_2 compared to BeF_2.

I have benefited from discussions with many colleagues working in the area of electron–polar molecule interactions. In particular, I wish to thank Professors A. Herzenberg and W. C. Lineberger. I also wish to acknowledge the contributions of my co-workers, Drs. Blickensderfer, Luken, Seeger, Simons, and Wendoloski.

[40] M. Krauss and D. Neumann, *Chem. Phys. Lett.*, **14**, 26 (1972); J. Pacansky, V. Wahlgren, and P. S. Bagus, *J. Chem. Phys.*, **62**, 2740 (1975); W. B. England, B. J. Rosenberg, P. J. Fortune, and A. C. Wahl, *ibid.*, **65**, 684 (1976).

Initial-State and Transition-State Solvent Effects on Reaction Rates and the Use of Thermodynamic Transfer Functions

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The past few years have seen greatly increased interest in the use of thermodynamic transfer functions by organic chemists. Their use to elucidate transition-state behavior started in the 1960s, on the one hand with Arnett's work[2] aimed to explain the serpentine variation of the hydrolysis of *tert*-butyl chloride in alcohol–water mixtures and on the other with Parker's studies[3] of bimolecular nucleophilic substitution reactions in dipolar aprotic solvents. The latter were found to have very large rate-enhancing properties in many instances as compared with hydroxylic solvents.[4]

Our own work with dipolar aprotic media[5] also started with the aim of bringing about certain reactions which could not readily be accomplished in hydroxylic solvents. Thus we found that deuterioxide-catalyzed H/D exchange in 1,3,5-trinitrobenzene occurred readily in dimethylformamide (DMF) rich media (e.g., 90:10 v/v $DMF–D_2O$),[6] whereas exchange by NaOD in D_2O alone was negligible. Some years later it became apparent to us that serendipity had played its role, as it was found that a competing equilibrium, σ-complex formation, was also greatly enhanced by the dipolar aprotic medium (vide infra).

An equal challenge was to find an explanation for the failure of an anticipated large rate increase to materialize. The OH^- catalyzed isotopic exchange of D_2 in $Me_2SO–H_2O$ mixtures might have been expected to result in very large rate increases. However, the observed[7] rate increase on changing the solvent from aqueous to 99.6 mol % Me_2SO was only 10^4, whereas the basicity of the medium as measured by the H_- function increases by 14 logarithmic units over this range.[8]

In this Account, we examine systematically the various possible outcomes of medium changes on rate processes as approached from the viewpoint of thermodynamic transfer functions.[9] This approach is highly informative concerning transition-state structure in a variety of processes, enabling one to deduce subtle effects of charge distribution, etc., and the correlation between medium effects and structure–reactivity relationships. Medium effects are generalized here in the widest sense, including, for example, the variation of acid concentration for reactions occurring in moderately concentrated acid media. Our purpose is not only to highlight recent developments but also to point to some future directions for the application of this method so as to provide an impetus for further research. Espe-

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Harold Wilson was born in England and studied at Sheffield University, where he obtained the B.Sc. and Dip. Ed. degrees. He taught in Canada for several years before continuing graduate study at Rice University, where he received the Ph.D. in 1971. Following postdoctoral work at Queen's University, he assumed his present position at John Abbott College. His research interests include the mechanism of proton transfer processes, ion pairing, and especially synergistic effects as probes in bioorganic and physical organic chemistry.

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[1] Address correspondence to E.B.

[2] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

[3] A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

[4] J. J. Delpuech, *Bull. Soc. Chim. Fr.*, 1624 (1966).

[5] E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, **14**, 133 (1977).

[6] E. Buncel and E. A. Symons, *Can. J. Chem.*, **44**, 771 (1966).

[7] E. A. Symons and E. Buncel, *J. Am. Chem. Soc.*, **94**, 3641 (1972).

[8] R. Stewart and J. P. O'Donnell, *Can. J. Chem.*, **45**, 911 (1967).

[9] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963.

0001-4842/79/0112-0042$01.00/0