

- (11) For a discussion of the states of O_2 see B. J. Moss and W. A. Goddard III, *J. Chem. Phys.*, **63**, 3523 (1975); B. J. Moss, F. W. Bobrowicz, and W. A. Goddard III, *ibid.*, **63**, 4632 (1975).
- (12) This is from Mulliken populations. Generally, these populations indicate a greater charge transfer than would be indicated, for example, by the dipole moment. Thus, the populations, although indicative of relative charge transfer, should not be taken too literally.
- (13) The discussion here is related to the approach used by C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, **5**, 45 (1970); *Theor. Chim. Acta*, **26**, 195, 211 (1972).
- (14) In Figures 4 and 6 we draw the $1^3\Pi$ and $2^3\Pi$ states as crossing. Actually, there is a matrix element connecting them which leads to a small energy gap and adiabatic states which do not cross.
- (15) E. I. Alessandrini and J. F. Freedman, *Acta Crystallogr.*, **16**, 54 (1963); G. W. C. Wyckoff, "Crystal Structures", 2nd ed, Interscience, New York, N.Y., 1964.
- (16) The spin eigenfunctions (SEFs) used are as follows. For the four-electron singlet

$$G1 = a[\phi_1\phi_2\phi_3\phi_4 \frac{1}{\sqrt{4}}\{(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)\}] = \begin{array}{|c|c|} \hline \phi_1 & \phi_2 \\ \hline \phi_3 & \phi_4 \\ \hline \end{array}$$

$$G2 = a[\phi_1\phi_2\phi_3\phi_4 \frac{1}{\sqrt{12}}\{2\alpha\alpha\beta\beta + 2\beta\beta\alpha\alpha - (\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)\}] = \begin{array}{|c|c|} \hline \phi_1 & \phi_3 \\ \hline \phi_2 & \phi_4 \\ \hline \end{array}$$

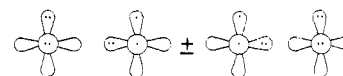
For the four-electron triplet

$$G1 = a[\phi_1\phi_2\phi_3\phi_4 \frac{1}{\sqrt{2}}\{(\alpha\beta - \beta\alpha)\alpha\alpha\}] = \begin{array}{|c|c|} \hline \phi_1 & \phi_2 \\ \hline \phi_3 & \\ \hline \phi_4 & \\ \hline \end{array}$$

$$G2 = a[\phi_1\phi_2\phi_3\phi_4 \frac{1}{\sqrt{6}}\{2\alpha\alpha\beta\alpha - (\alpha\beta + \beta\alpha)\alpha\alpha\}] = \begin{array}{|c|c|} \hline \phi_1 & \phi_3 \\ \hline \phi_2 & \\ \hline \phi_4 & \\ \hline \end{array}$$

$$G3 = a[\phi_1\phi_2\phi_3\phi_4 \frac{1}{\sqrt{12}}\{3\alpha\alpha\alpha\beta - (\beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta)\alpha\}] = \begin{array}{|c|c|} \hline \phi_1 & \phi_4 \\ \hline \phi_2 & \\ \hline \phi_3 & \\ \hline \end{array}$$

- where horizontally coupled orbitals indicate that the spin function is asymmetric under interchange of a and b , while vertically coupled orbitals indicate that the spin function is symmetric under interchange of a and b .
- (17) Since the SEFs are orthogonal, states corresponding to different spin eigenfunctions (SEFs) can at most be coupled by transpositions arising from the antisymmetrizer. The resulting matrix elements involve two-electron exchange integrals and are generally smaller than for cases where the two states have the same SEF (in which case they can have one-electron terms connecting them, if they differ by only a single excitation).
- (18) C. F. Melius, B. D. Olafson, and W. A. Goddard III, *Chem. Phys. Lett.*, **28**, 457 (1974); C. F. Melius and W. A. Goddard III, *Phys. Rev. Sect. A*, **10**, 1528 (1974).
- (19) A. J. H. Wachters, *J. Chem. Phys.*, **52**, 1033 (1970).
- (20) T. A. Smedley and W. A. Goddard III, unpublished calculations. Similar effects have been observed by Brooks and Schaefer for the Mn atom (ref 21).
- (21) B. R. Brooks and H. F. Schaefer III, "A Model Transition Metal-Carbene System $MnCH_2$ ", to be published.
- (22) T. H. Dunning, Jr., and P. J. Hay in "Modern Theoretical Chemistry: Methods of Electronic Structure Theory", Vol. 3, H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1977. The p functions are the same as in ref 23, the tightest seven s functions are contracted into a single s function based on the 1s HF orbital, the second and third most diffuse are contracted into a basis function based on the 2s HF orbital, and the most diffuse function is uncontracted.
- (23) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
- (24) P. J. Hay and T. H. Dunning, Jr., *J. Chem. Phys.*, **64**, 5077 (1976).
- (25) The group II states of NiO are analogous to the Shumann-Runge states of O_2 which involve transfer of one electron from one oxygen atom to the other in the σ system coupled with transfer of a second electron in the opposite direction in the π system. Thus, we refer to the group II states as charge



transfer states relative to the group I states even though both sets of states arise from neutral atomic configurations.

Dissociation Energies, Electron Affinities, and Electronegativities of Diatomic Molecules. An Empirical Correlation with Predictions for XY , XY^+ , and XY^-

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Abstract: Experimental dissociation energies D_0 of diatomic molecules containing elements from Li to F and Na to Cl have been correlated empirically by imagining a continuous two-dimensional function in atomic-number space. Contours of constant $D_0(XY)$ and $D_0(XY^+)$ show remarkable similarities that allow prediction of dissociation energies of uninegative ions XY^- . From $D_0(XY^+)$ and $D_0(XY^-)$, electronegativities and electron affinities of XY are calculated for diatoms of Li to F. The method is readily extended to other elements.

Introduction

Dissociation energies $D_0(XY)$ of many diatomic molecules XY have been determined, some with exceptional accuracy. Recent lists¹ of such values seem to reach a best or recommended value by thorough study of all data for a particular diatom with perhaps some subjective estimate of general reasonableness or physical limits in the background. The mass of data that are reliable has grown through the years until now, for diatoms made of elements from Li to F and from Na to Cl, only a relatively few values remain absent.

This paper presents an empirical correlation of the D_0 s of Tables I and II. All the values are experimental. It seemed best from the start to exclude all calculated values, not because all

are unreliable, but merely because there is a clear distinction between what is observed and what is calculated. However, in accord with theory, the elusive $D_0(Be_2)$ has been assumed to be essentially zero, as have D_0 s for all diatoms with four valence electrons.

Computational Details

Tables I and II list D_0 s by atomic numbers of the atoms. When these values are listed in square arrays according to atomic number, regular trends are evident. Irregularities, obvious in the array, are expected theoretically because of the quantized energies of both atoms and molecules, yet it is possible to find effectively continuous contours of constant energy.

Table I. Selected Values of Dissociation Energies from the Lowest Vibrational State

Diatom	D_0 , eV	Ref	Diatom	D_0 , eV	Ref	Diatom	D_0 , eV	Ref
LiLi	1.11 ± 0.01	<i>d</i>	LiCl	4.90 ± 0.15	<i>a,d</i>	NaNa	0.79	<i>b</i>
LiN	~2.1	<i>f</i>	BeS	3.8 ± 0.6	<i>a</i>	NaCl	4.27 ± 0.02	<i>b</i>
LiO	3.35 ± 0.22	<i>b</i>	BeCl	3.98 ± 0.13	<i>b,d</i>	MgMg	0.0495 ± 0.0007	<i>d</i>
LiF	5.95 ± 0.20	<i>d</i>	BS	6.11 ± 0.17	<i>c</i>	MgS	1.72 ± 0.35	<i>c</i>
BeBe	0.00	<i>g</i>	BCl	5.51 ± 0.17	<i>b</i>	MgCl	3.20 ± 0.44	<i>b</i>
BeN	~3.9	<i>b</i>	CSi	4.47 ± 0.22	<i>a</i>	AlAl	1.64	<i>p</i>
BeO	4.61 ± 0.13	<i>b</i>	CP	5.28 ± 0.10	<i>e</i>	AlSi	2.44 ± 0.30	<i>q</i>
BeF	5.9 ± 0.2	<i>a,d</i>	CS	8.04 ± 0.10	<i>d</i>	AlP	2.21 ± 0.13	<i>a</i>
BB	3.02 ± 0.28	<i>b</i>	CCl	3.43 ± 0.22	<i>b</i>	AlS	3.73 ± 0.13	<i>d</i>
BN	5.68	<i>b</i>	NAI	3.73 ± 0.87	<i>b</i>	AlCl	5.13 ± 0.04	<i>b</i>
BO	8.29 ± 0.10	<i>b,d</i>	NSi	5.66 ± 0.65	<i>b</i>	SiSi	3.17 ± 0.13	<i>b</i>
BF	7.73 ± 0.14	<i>b</i>	NP	7.23 ± 0.05	<i>b</i>	SiS	6.44 ± 0.13	<i>c</i>
CC	6.11 ± 0.04	<i>b,d</i>	NS	5.0 ± 0.7	<i>a,b</i>	SiCl	3.90 ± 0.65	<i>b</i>
CN	7.76 ± 0.11	<i>b</i>	NCl	4. ± 0.5	<i>a</i>	PP	5.033 ± 0.005	<i>a,b,d</i>
CO	11.09 ± 0.02	<i>a,b,d</i>	ONa	2.6 ± 0.2	<i>e</i>	PS	4.54 ± 0.10	<i>r</i>
CF	5.6 ± 0.1	<i>d</i>	OMg	4.04 ± 1.5	<i>j</i>	SS	4.38 ± 0.02	<i>a,b,d</i>
NN	9.76 ± 0.005	<i>a,b,d</i>	OAl	5.14 ± 0.11	<i>k</i>	ClCl	2.479 ± <0.001	<i>a,b,d</i>
NO	6.50 ± 0.01	<i>a,d</i>	OSi	8.2 ± 0.04	<i>l</i>			
NF	3.3 ± 0.5	<i>h</i>	OP	6.13 ± 0.15	<i>c</i>			
OO	5.115 ± 0.002	<i>a,d</i>	OS	5.40 ± 0.01	<i>c</i>			
OF	2.20 ± 0.10	<i>i</i>	OCl	2.746 ± 0.001	<i>a</i>			
FF	1.60 ± 0.05	<i>a</i>	FNa	5.33 ± 0.13	<i>m</i>			
			FMg	4.61 ± 0.06	<i>b</i>			
			FAI	6.90 ± 0.03	<i>b</i>			
			FSi	5.64 ± 0.13	<i>b</i>			
			FP	4.65 ± 0.2	<i>n</i>			
			FS	3.51 ± 0.05	<i>o</i>			
			FCl	2.558 ± 0.001	<i>a</i>			

^a Reference 1a. ^b Reference 1b. ^c Reference 1c. ^d Reference 1d. ^e Reference 1e. ^f R. R. Herm and D. R. Herschbach, *J. Chem. Phys.*, **52**, 5783 (1970). ^g G. C. Lie and E. Clementi, *ibid.*, **60**, 1288 (1974). ^h Mean of JANAF value and 3.5 ± 0.3 from P. A. G. O'Hare, *ibid.*, **59**, 3842 (1973); P. A. G. O'Hare and A. C. Wahl, *ibid.*, **54**, 4563 (1971). ⁱ K. O. Mac Fadden and E. Tschuikow-Roux, *J. Phys. Chem.*, **77**, 1475 (1973). ^j P. J. Evans and J. C. Mackie, *Chem. Phys.*, **5**, 277 (1974). ^k D. L. Hildenbrand, *Chem. Phys. Lett.*, **20**, 127 (1973). ^l Reference 1 and H. Bredohl, R. Cornet, I. Dubois, and F. Remy, *J. Phys. B*, **7**, L66 (1974). ^m D. O. Ham, *J. Chem. Phys.*, **60**, 1802 (1974). ⁿ P. A. G. O'Hare, *ibid.*, **59**, 3842 (1973). ^o D. L. Hildenbrand, *J. Phys. Chem.*, **77**, 897 (1973). ^p 1.73 ± 0.16 from C. Chatillon, M. Allibert, and A. Pattoret, *C. R. Acad. Sci., Ser. C*, **280**, 1505 (1975), averaged with 1.55 ± 0.15 from J. Drowart et al., *High Temp. Sci.*, **5**, 482 (1973). ^q 2.33 ± 0.31 from C. A. Stearns and F. J. Kohl, *High Temp. Sci.*, **5**, 113 (1973), averaged with 2.56 ± 0.12 from C. Chatillon et al. (see *p*). ^r J. Drowart et al., *ibid.*, **5**, 482 (1973).

These are shown in Figures 1–4 at levels of 0, 2, 4, 6, 8, and 10 eV, with 0 eV taken for species isoelectronic with Be₂. With only empirical guidance, the contours have been drawn as though a "sharp" ridge (cusp?) exists at the ten-electron line. Whether this ridge should be more rounded is a matter for theoretical study beyond this paper.

A general lack of D_{0s} suggests that contours not be attempted without some extra guidance for unipositive diatoms XY⁺ containing elements from Na to Cl. When, along any line in the array, three or more D_{0s} show a trend, these were plotted to find a fractional position in atomic-number space where D_0 would be 0, 2, 4, . . . , eV. Generally, however, only linear interpolation between values could be used to locate points which together guided the choice of contour position of constant D_0 in Figures 1–4. As already noted, quantum effects cause irregularities which prohibit use of contours close in energy, although near Li₂ and Na₂ a closer spacing could perhaps be useful since D_0 is small in this region.

The contours were drawn through such points by eye as the best and simplest compromise. A computer program requiring a complete array of D_{0s} was used with arbitrarily set D_{0s} where experimental values were lacking. Qualitatively equivalent contours resulted. Hence, the "by eye" method seems acceptable. Dashed contours indicate a lack of data or some uncertainty in position.

Discussion

A glance at Figures 1–4, each drawn independently, shows remarkable similarities. The energy difference between contours seems to be great enough to span and overlook the ex-

Table II. Selected Values of Dissociation Energies of Unipositive Diatomic Molecules in the Lowest Vibrational State

Diatom	D_0 , eV	Ref
LiLi ⁺	1.55 ± 0.15	<i>a</i>
BeO ⁺	3.5 ± 0.3	<i>a</i>
BeF ⁺	6.1 ± 0.8	<i>e</i>
BF ⁺	5.0 ± 0.2	<i>e</i>
CC ⁺	5.22 ± 0.1	<i>e</i>
CN ⁺	4.97 ± 0.11	<i>e</i>
CO ⁺	8.34 ± 0.03	<i>a,d</i>
CF ⁺	7.61 ± 0.05	<i>c</i>
NN ⁺	8.72 ± 0.01	<i>d</i>
NO ⁺	10.86 ± 0.04	<i>a,d</i>
NF ⁺	~5.24	<i>a</i>
OO ⁺	6.67 ± <0.01	<i>e</i>
OF ⁺	3.05	<i>f</i>
FF ⁺	3.32 ± 0.03	<i>e</i>

^a Reference 1a. ^b Reference 1b. ^c Reference 1c. ^d Reference 1d. ^e Reference 1e. ^f P. M. Dehmer and W. A. Chupka, *J. Chem. Phys.*, **59**, 925 (1973).

pected quantum effects, which should be most evident for the atoms and molecules made of Li to F. The persistence of the ten-electron maximum in D_0 , emphasized by a dashed straight line, is striking. Clearly the ideas of simple MO theory in which electrons are in bonding and antibonding orbitals and isoelectronic arrangements are of paramount importance. Such regularity in pattern is a pleasant surprise in view of the paucity of points, and it suggests that D_{0s} can be predicted roughly by

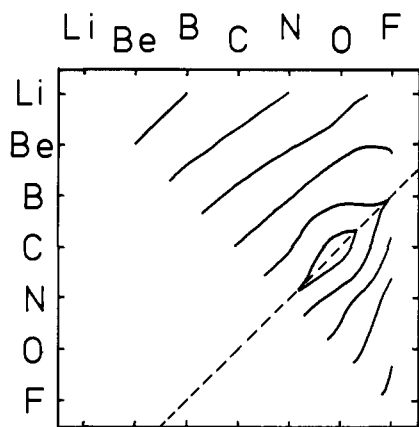


Figure 1. Dissociation energies $D_0(XY)$ for diatoms of Li to F. (Contours at 10, 8, 6, 4, 2, and 0 eV.)

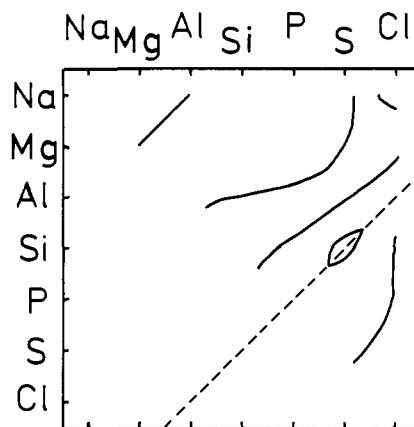


Figure 3. Dissociation energies $D_0(XY)$ for diatoms of Na to Cl. (Contours at 6, 4, 2, and 0 eV.)

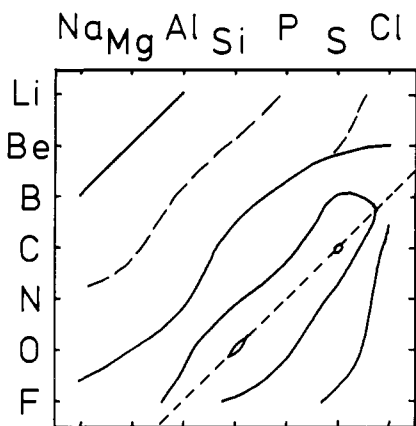


Figure 2. Dissociation energies $D_0(XY)$ for diatoms of Li to F with Na to Cl. (Contours at 8, 6, 4, 2, and 0 eV.)

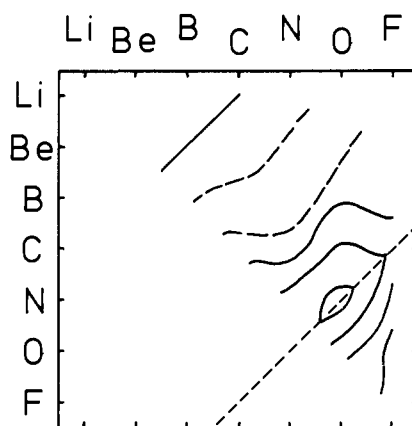


Figure 4. Dissociation energies $D_0(XY^+)$ for unipositive diatoms of Li to F. (Contours at 10, 8, 6, 4, 2, and 0 eV.)

such diagrams, which presumably turn whatever systematic trends exist toward a best guess for a D_0 as yet unmeasured. For example, Figure 1 would make $D_0(\text{LiC})$ equal about 1 eV, with $D_0(\text{BeB}) \approx 1.3$ eV, $D_0(\text{BeC}) \approx 2.5$ eV, $D_0(\text{BeN}) \approx 3.8$ eV, and $D_0(\text{BC}) \approx 4.4$ eV. In this sense, these figures have straightforward empirical use, just as rate laws do in chemical kinetics, whether or not the mechanism is known.

The asymmetry of Figure 2 suggests that increasing ionic character raises D_0 by about 1 eV. In every figure, in fact, the maximum D_0 s lie well off diagonal where nuclei have equal charge. It is possible that a set of ten valence electrons (in CO, CS, SiO, and SiS) has more stability when polarized, but it is also clear that atoms of N and P in their ground states show a special stability relative to ground states of C and O and Si and S. This would tend to generate depressions for D_0 s of molecules containing N and P, and the saddle points at N_2 , PN, and P_2 are the results. In view of the problems² associated with finding valence-state energies of atoms, it seems wise here to accept gratefully the general smoothness of Figures 1-4 without introducing exotic corrections in an attempt to get still further smoothness by considering dissociation to atoms in valence states.

Unlikely looking contours or difficulty in positioning them suggests big quantum effects or D_0 s that do not fit well the trend of neighbors. Some examples involve MgCl and LiCl.

An interesting general observation in Figures 1-4 is the steeper decline in D_0 on the side of the ten-electron line where antibonding electrons are added than on the side where bonding electrons are being removed as one leaves the maximum. The spectacular fall in D_0 from CO to NO and from CO

to CF thus is seen as a general trend in the figures and not an anomaly in low D_0 s of NO and CF.

A Universal Grid. The remarkable similarity of Figures 1-4 suggests that they all be correlated to yield an idealized contour grid or grille of universal use. As in spectroscopic states and chemical activity, the electronic state is the key. This same dominant role is shown here in that the contours of Figure 4 closely follow those of Figure 1 when the figures are superimposed: CO^+ upon BO, CN^+ upon BN, and of course the ten-electron lines superimposed. Only NO^+ and BeB^+ dissociate conventionally to an atom and an ion of higher atomic number. With NO^+ already at the very maximum, a change wherein NO^+ goes (contrary to convention) to N^+ and O with $D_0 = 11.79$ eV neither moves the maximum nor disrupts contours with the general displacement of Figure 4 relative to Figure 1 (with C^+ over B, O^+ over N, and so on). Of course, the contours of Figure 4 are abbreviated as if Figure 1 has an extra region along the diagonal for equal atomic numbers.

A displacement opposite to that for XY^+ relative to XY would yield estimates of $D_0(\text{XY}^-)$. It happens that even the magnitudes of D_0 on the contour grids for $D_0(\text{XY})$ and $D_0(\text{XY}^+)$ are essentially unchanged. With the nature of the electrons still of paramount importance, a stroke of the pen gets $D_0(\text{XY}^-)$, $D_0(\text{XY})$, and $D_0(\text{XY}^+)$ via just one figure (Figure 5), where the shapes of the contours are a "by-eye" mean of those in Figures 1 and 4. Thus, Figure 5 represents a kind of universal template for D_0 s of diatomic molecules containing Li to F. Finally, to the extent that electron affinities, ionization potentials, and the like are well behaved and that the contours retain their relative energy values, Figure 5 could be extended

Table III. A Comparison of Accepted Experimental Dissociation Energies to Values Predicted on the Basis of Isoelectricity

Anion	D_0 , eV		Cation	D_0 , eV		Cation	D_0 , eV	
	Ref 1	Pred		Ref 1	Pred		Ref 1	Pred
OO ⁻	4.08 ± 0.02 b	3.2	BCl ⁺	2.4 ± 0.7 a,b ^a	6.0	MgCl ⁺	3.63 ± 0.9 b	4.0
LiO ⁻	[3.44 ± 0.7] b	3.5	CS ⁺	6.69 ± 0.12 e	5.5	AlCl ⁺	1.77 ± 0.43 b	3.5
CC ⁻	8.86 ± 0.9 b	8.2	AlO ⁺	1.62 ± 0.6 b	4.0	PP ⁺	4.5 ± 1. a	4.5
CN ⁻	10.3 ± 0.13 b,c	9.	PO ⁺	9. ± 2. a	8.0	PS ⁺	6.6 ± 2. a	6.5
			SO ⁺	5.50 ± 0.06 e	6.0	SS ⁺	5.37 ± 0.04 e	5.0
			ClO ⁺	4.7 ± 0.2 e	5.0	ClCl ⁺	4.00 ± 0.05 a,d	3.5
			MgF ⁺	4.7 ± 0.3 e	4.5			
			AlF ⁺	3.24 ± 0.5 b	5.2			
			SiF ⁺	6.5 ± 0.3 e	7.0			
			PF ⁺	6.7 ± 2. a	5.0			

^a A compromise.

Table IV. Predicted Electron Affinities (in Brackets, eV) and Electronegativities of Some Diatomic Molecules

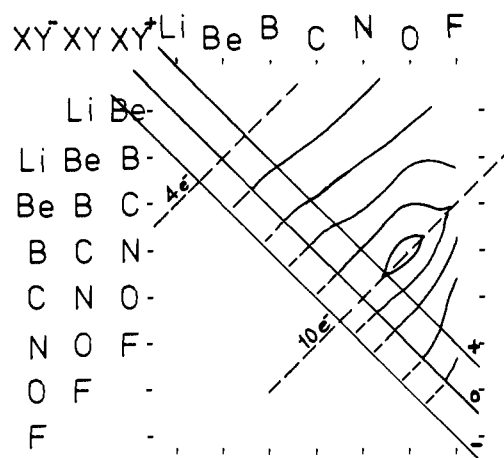
	Li	Be	B	C	N	O	F
Li			[2.1]	[2.7]	[2.2]	[3.5]	[4.5]
				4.6	4.4	5.0	5.4
Be		[1.5]	[1.8]	[3.0]	[1.0]	[4.0]	[5.8]
			5.8	6.8	5.8	7.6	8.0
B			[1.8]	[3.2]	[3.1]	[4.0]	[1.5]
			5.7	6.6	6.6	7.4	
C				[3.0]	[2.0]	[-1.8]	[1.2]
				8.1	7.9		5.2
N					[-2.0]	[-0.7]	[2.5]
						4.8	7.4
O						[-0.3]	[2.5]
						5.6	9.5
F							[3.0]
							9.8

to XY²⁻, XY²⁺, and so on. However, as the net charge of the diatom deviates more and more from zero, points on the standard grid of contours should perhaps be projected from the point at zero atomic number along lines with the ratio of atomic numbers Z_X/Z_Y constant so that the addition or loss of electrons can be effected without change in the polarity of the electron groupings. Such a projection, not attempted here, would incur distortions in the universal contour grid. Figures 1 and 4 suggest such distortions to be unimportant for the minor change XY⁻ relative to XY.

Straightforward extension of Figures 2 or 3 to isoelectronic and isoperiodic diatoms such as BCl⁺ and PP⁺ (in the same spirit by which Figure 5 stems from Figures 1 and 4) permits predictions of D_0 s. Table III compares these empirical predictions to the accepted experimental values. The agreement is within expected limits except for BCl⁺ and species containing Al. (An interesting problem is also whether $D_0(\text{BO}^-)$ exceeds $D_0(\text{CN}^-)$, as Figure 5 suggests.)

The dissociation energy of F₂⁻ is predicted at the very edge of Figure 5 to be less than 2 eV, probably about 1 eV. The value predicted by calculation³ is 1.06 eV or a bit more. Indeed, the outer reaches of the contours of Figure 5 might be considerably extended if still more calculated D_0 s for species like NeF⁺ and Ne₂⁺ were to be mixed with the observed values.

These five figures have been drawn as if a near cusp exists along the ten-electron line. (A theoretical discussion of how sharp that ridge might be would be welcome.) One theoretical problem that Figure 1 does, however, illumine is double minimum in N₃. Calculation⁴ finds N₃ to be linear but unsymmetrical. If something about N₃ can be understood in terms of diatoms, then the question is whether a lower molecular energy (higher D_0) is to be attained by distortions that climb the ionic routes from N₂ to CO at the saddle point in Figure

**Figure 5.** Standard contours of equal dissociation energy for diatoms XY⁺, XY, and XY⁻ for Li to F. (Contours at 10, 8, 6, 4, 2, and 0 eV.)

1 or by maintaining nonionic bonding (presumably equivalent bonds) by adhering to the diagonal of equal atomic numbers in Figure 1. Presumably, electrons in each bond in N₃ partake of polarization (up the saddle) because the rate of rise exceeds the rate of loss at the saddle point at N₂. As noted above, this could make the asymmetry of N₃ and its low D_0 depend on the circumstance that N (and P) have very stable atomic electronic states.

Electronegativities and Electron Affinities. With atomic ionization potentials and atomic electron affinities known, diagrams like these yield effective electronegativities of pairs of atoms. The method of Iczkowski and Margrave⁵ requires at least the energies of XY⁺, XY, and XY⁻. The generally crucial item is a value for $D_0(\text{XY}^-)$, now available for many diatoms via figures like Figure 5. With data from the JANAF tables,^{1b} one readily finds that the electronegativities of CN, CC, OH, and OO are 8.96, 7.93, 7.50, and 6.25 on a scale where F, O, N, . . . are 12.46, 9.42, 7.39, With Figure 5 and the like, many diatomic electronegativities can now be found. These may have chemical significance in understanding molecules in terms of pairs of atoms within them. For example, C₂ resembles oxygen atom,⁶ as found also here.

It is a straightforward exercise in the use of Figure 5 and the methods of Iczkowski and Margrave to calculate electronegativities of many diatoms. Along the way, electron affinities (EA) of the diatoms also happen. Both are reported in Table IV, with EA in eV in brackets. Assumed in this calculation were the atomic EA of Gaydon:^{1a} B (0.3); C (1.2); N (0.0); O (1.5); F (3.5). It is nice to see, for the diatoms having negative EAs, that they increase thus: N₂ (-2.0); CO (-1.8); NO (-0.7); Values of electronegativity are not reported for N₂, CO, and BF because it is likely that the energies of these

diatoms and their ions are not continuous as a function of electron population, as required.⁵ The general trend in electronegativities follows chemical experience with high values for BeF, CC, CN, OF, and FF. These may be of use in understanding relationships among parts of larger molecules.

Extension of these methods to diatoms containing Na to Cl is merely an exercise. Finding more D_{0s} of good accuracy for XY and XY^+ will allow diatoms of elements beyond Ar to be dealt with thus.

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Structure of Fluoromethyl Radicals. Conjugative and Inductive Effects

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Abstract: Factors determining the geometry of CH_nX_{3-n} radicals are illuminated on the basis of one-electron MO (OEMO) theory. Inductive and conjugative effects are found to be operative in fluoromethyl radicals ($X = F$). The relative importance of these two effects is discussed. The qualitative conclusions are supported by ab initio calculations of the fluoromethyl radicals.

The geometry of the methyl radical has been probed by means of a variety of spectroscopic,² chemical,³ and theoretical⁴ methods. The consensus is now that this radical exists in a near-planar geometry, the deviation from planarity being small and much dependent on the experimental technique or the sophistication of the quantum-mechanical calculation. A much more pronounced trend which has been revealed by spectroscopic methods is the progressive increase in the pyramidalization of the methyl radical as each hydrogen is successively replaced by a more electronegative first period atom such as F, O, etc.² The origin of this effect can be understood by focusing attention on the following two electronic factors: (a) the σ inductive effect of the electronegative atom⁵ and (b) the π conjugative effect of the electronegative atom. The mode of operation of the σ inductive effect in dictating the bond angles of molecules has been discussed recently, using a simple MO approach.⁶ It was argued that the bending of a linear AB_2 molecule or pyramidalization of a planar AB_3 molecule will tend to occur if such a geometric change allows substantial mixing of the highest occupied π MO (HOMO) with the lowest unoccupied σ MO (LUMO). Specifically, it was demonstrated that in cases where A is a second-row element or when B is an electronegative atom, such mixing becomes substantial owing to a decreasing HOMO-LUMO energy gap. The basic arguments can be easily applied to the problem at hand, as discussed below.

Consider the planar methyl radical whose MO's are shown in Figure 1. Upon pyramidalization, the symmetry of the molecule is relaxed from D_{3h} to C_{3v} . This allows Ψ_4 (i.e., the singly occupied MO) to mix with Ψ_1 and Ψ_5 . Now, the Ψ_1 - Ψ_4 interaction results in stabilization or destabilization, depending

on several factors (vide infra). However, this effect is small and may be neglected.⁷ The Ψ_4 - Ψ_5 interaction always results in stabilization and, consequently, favors the nonplanar geometry. As the electronegativity of the substituents is increased, the energy of Ψ_5 decreases. This effectively decreases the Ψ_5 - Ψ_4 energy gap and increases the strength of the interaction between these orbitals. Consequently, as the electronegativity of the substituents is increased, the preference for nonplanarity should increase.

On the basis of the above model which focuses exclusively on the substituent inductive effect, the following specific predictions can be made.

(a) The pyramidalization of the radical center will increase in the order $\dot{C}X_3 > \dot{C}X_2H > \dot{C}XH_2$, where X is a σ inductively withdrawing group.

(b) Charge transfer from the radical center to the heteroatom X will occur upon pyramidalization, and its magnitude will vary in the order $\dot{C}X_3 > \dot{C}X_2H > \dot{C}XH_2$. Accordingly, the C-X bond in all three radicals will acquire greater ionic character as the planar form is transformed to a pyramidal form, the effect being greatest for $\dot{C}X_3$.

The π conjugative effect refers to the interaction of the " π " lone pair of X with the singly occupied carbon AO, and it can have important conformational consequences. We shall utilize a one-electron MO (OEMO) approach with inclusion of overlap to investigate the effect of conjugation in substituted methyl radicals, and our approach will be illustrated by reference to the model systems CH_2F , CHF_2 , and CF_3 .

The π -type MO's of the planar substituted methyl radicals can be constructed by mixing the C p_z AO with the appropriate group MO's (GMO's) spanning the F p_z AO's. The fluorine