or Pt onto the outermost surface as has been done with p-Si.[15a]

A final interesting point concerning p-WS_2 is that the photocurrent–voltage data for H_2 evolution in strong acid solution suggests that the photoelectrolysis of HBr according to eq 3 and 4 would be possible by using a cell employing a p-WS_2 photocathode and an n-WS_2 photoanode.

$$2H^+ + 2e^- \rightarrow H_2 \text{ (at p-WS}_2\text{ photocathode)} \tag{3}$$

$$2Br^- + 2h^+ \rightarrow Br_2 \text{ (at n-WS}_2\text{ photoanode)} \tag{4}$$

Indeed, the data[8] from Br^- photooxidation show that the n-WS_2 electrode gives its η_{max} at a potential where Pd-treated p-WS_2 gives its η_{max} for H_2 evolution, $\sim$+0.3 V vs. SCE. Thus, visible illumination of the n-WS_2 shorted to the Pd-treated p-WS_2 should give good efficiency for the generation of Br_2 and H_2, respectively, from HBr. A similar double photoelectrode-based cell, p-InP/n-WSe_2, has recently been reported.[43] We find maximum initial efficiencies of >5% with 632.8 nm illumination at 20–40 mW/cm^2 are obtained under short-circuit conditions for a two compartment cell with aqueous 6 M H_2SO_4/2 M LiBr electrolyte in both compartments. Br_2, $\sim$2 mM, was added to the photoanode compartment to poise the half-cell potential. Illumination intensities were adjusted until a small reduction in the intensity at either photoelectrode gave an equivalent decrease in full cell current. Unfortunately, while we have uncovered a situation where both the n- and p-type semiconductors should give optimum performance in the same medium, the WS_2 double photoelectrode-based cell for HBr electrolysis rapidly loses efficiency, owing to deterioration in performance of the photocathode. This result underscores the need to elaborate the conditions under which good performance for n- and p-type semiconductor electrodes can be simultaneously sustained.

Conclusions

Single-crystal p-type WS_2 photocathodes have a good wavelength response ($E_g \approx 1.3$ eV), a good output photovoltage (up to $\sim$0.8 V), and are durable in a variety of solvent/electrolyte/redox couple combinations. Demonstrated overall efficiencies for the sustained conversion of 632.8-nm light to electricity exceeds 7%, and Pd- or Pt-treated p-WS_2-based cells evolve H_2 from acidic solutions with similar ($\sim$7%) efficiency at input visible light power densities of >50 mW/cm^2. The p-WS_2 is relatively free of surface states that would cause Fermi level pinning. A key point supporting this is that the dark oxidation of reduced species generally occurs positive of E_{FB} for couples having $E_{1/2}$ in a potential regime where the surface is not inverted. Over a wide range of E_{redox}, the p-WS_2 behaves ideally in that the photovoltage depends on E_{redox} in a manner consistent with a surface state-free interface. Sufficiently negative E_{redox} is associated with carrier inversion and, ultimately, junction breakdown of the WS_2/liquid interface. Good agreement is obtained between interfacial energetic measurements from cyclic voltammetry, interface capacitance, and steady-state photocurrent–voltage curves.

Acknowledgment. Work at M.I.T. was supported by GTE Laboratories, Inc., and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences. D.J.H. acknowledges support as an NSERC Fellow, 1980–present, and A.J.R. acknowledges support as an NPW Fellow, 1982–1983.

Registry No. WS_2, 12138-09-9; H_2, 1333-74-0; H_2O, 7732-18-5; Pd, 7440-05-3; Pt, 7440-06-4; $[MPT]^{+\cdot}$, 34510-35-5; MPT, 1207-72-3; $[TMPD]^{2+}$, 34527-56-5; $[TMPD]^{+\cdot}$, 34527-55-4; $[TTF]^{2+}$, 35079-57-3; $[TTF]^{+\cdot}$, 35079-56-2; $[Fe(\eta^5\text{-}C_6H_5)(\eta^5\text{-}C_5H_4CH_2N(CH_3)_3)]^{2+}$, 51150-57-3; $[Fe(\eta^5\text{-}C_6H_5)(\eta^5\text{-}C_5H_4CH_2N(CH_3)_3)]^{+}$, 33039-48-4; TTF, 31366-25-3; TCNE, 670-54-2; $[TCNE]^{-\cdot}$, 34512-48-6; TCNQ, 1518-16-7; $[TTNQ]^{-\cdot}$, 34507-61-4; $[TCNQ]^{2-}$, 48161-40-6; $[MV]^{2+}$, 4685-14-7; $[MV]^{+}$, 25239-55-8; $Ru(acac)_3$, 14284-93-6; $[Ru(acac)_3]^-$, 66560-52-9; MV, 25128-26-1; BAQ, 84-47-9; $[BAQ]^{-\cdot}$, 77898-33-0; $[BAQ]^{2-}$, 84878-05-7; $[IrCl_6]^{2-}$, 16918-91-5; $[IrCl_6]^{3-}$, 14648-50-1; $[Mo(CN)_8]^{3-}$, 17845-99-7; $[Mo(CN)_8]^{4-}$, 17923-49-8; $[Fe(CN)_6]^{3-}$, 13408-62-3; $[Fe(CN)_6]^{4-}$, 13408-63-4; $[Ru(NH_3)_6]^{3+}$, 18943-33-4; $[Ru(NH_3)_6]^{2+}$, 19052-44-9; $[Ru(NH_3)_6Cl_3]$, 14282-91-8; H_2SO_4, 7664-93-9; I_3^-, 14900-04-0; I^-, 20461-54-5; $[\text{thianthrene}]^{+\cdot}$, 34507-27-2; thianthrene, 92-85-3; [1,1′-diacetylferrocene]$^+$, 12277-02-0; 1,1′-diacetylferrocene, 1273-94-5; [acetylferrocene]$^+$, 32662-25-2; acetylferrocene, 1271-55-2; [ferrocene]$^+$, 12125-80-3; ferrocene, 102-54-5; chloranil, 118-75-2; [chloranil]$^{-\cdot}$, 17217-66-2; [decamethylferrocene]$^+$, 54182-41-1; decamethylferrocene, 12126-50-0; [chloranil]$^{2-}$, 55976-90-4; $[Ru(2,2'\text{-bipyridine})_3]^{2+}$, 15158-62-0; $[Ru(2,2'\text{-bipyridine})_3]^{+}$, 56977-24-3; $Ru(2,2'\text{-bipyridine})_3$, 74391-32-5; $[Ru(2,2'\text{-bipyridine})_3]^-$, 56977-23-2; KCl, 7447-40-7.

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(43) Levy-Clement, C.; Heller, A.; Bonner, W. A.; Parkinson, B. A. *J. Electrochem. Soc.* **1982**, *129*, 1701.

Non-Koopmans' Theorem Effects in the He I Photoelectron Spectra of Polyenes

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Abstract: The predictions of the Koopmans' theorem MNDO model and the non-Koopmans' theorem (NKM) model for the photoelectron spectra of *p*-quinodimethane and its 2,5-dimethyl and perfluoro derivatives are discussed. The results of HAM/3-CI calculations support the NKM interpretation and indicate the weak feature at 13.4 eV in the PE spectrum of 1,1,4,4-tetrafluorobutadiene can be assigned to the lowest KTM "forbidden" transition in this case.

Dewar has recently[1] provided a critical discussion of our experimental results and of our interpretation of the He I photoelectron spectra of *p*-quinodimethane (**1**)[2] and its 2,5-dimethyl derivative (**2**).[3] In doing so he has provided an excellent focus on the question of the applicability of Koopmans' theorem[4] as an interpretive model (KTM) for the UV-PE spectra of such compounds. As Dewar points out, a distinction between the KTM

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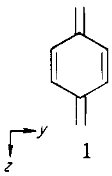
(1) Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 1447.

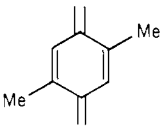
(2) Koenig, T.; Wielesek, R. A.; Snell, W.; Balle, T. *J. Am. Chem. Soc.* **1975**, *97*, 3225.

(3) Koenig, T.; and Southworth, S. *J. Am. Chem. Soc.* **1977**, *99*, 2807.

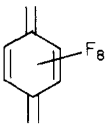
(4) Koopmans, T. *Physica (Utrecht)* **1934**, *1*, 104.



1



2



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and our non-Koopmans' interpretation (NKM) is important and we believe it can be provided by suitable experimental investigations. (We presently use the language of molecular-orbital theory though our original discussion[2] of the spectrum of **1** was in terms of the structure-representation basis.) However, it is necessary to remove some misrepresentations of the NKM that are present in the Dewar rendition so that the stage can be properly set for an experimental resolution of the question. We presently wish to provide the necessary clarification and to report some results of HAM/3-CI[5a] calculations on ionic states on even alternate polyenes and their derivatives.

We agree with Dewar in his statement that "no ionization can be forbidden".[1] However, *our* use of the term "forbidden" was referenced to the situation implicit in the KTM which Dewar adopts. That model assumes the neutral ground-state wave function is represented by a single configuration ($\psi^0 = \psi(i^2\ldots j^2\ldots k^2)$, $i - k$ occupied molecular orbitals). Each PE accessible ionic state is also taken as being expressible by a single configuration in which one of the doubly occupied orbitals has become singly occupied ($\psi_j^+ = \psi(i^2\ldots j^1\ldots k^2)$) with the added restriction that the molecular orbitals of the ion are identical with those of the neutral precursor (frozen orbital approximation). In the KTM, each observed π PE band is thus associated with promotion of a single electron from the appropriate doubly occupied set ($i - k$) of the neutral system to the free-electron function (f). All of these single-particle excitations are "allowed" without regard to symmetry of the orbital being vacated. The cross sections for transitions to this highly restricted group of the π-ionic states are expected to be nearly constant (with He I radiation) since variations in proximity to their respective thresholds are not very large. The ratio of areas among the π PE spectral bands should thus be close to unity in the KTM as shown in eq 1, where A denotes area, T

$$\frac{A_a}{A_1} = \left[\frac{\langle f|T|j\rangle}{\langle f|T|k\rangle}\frac{\langle i^2\ldots j^1\ldots k^2|i^2\ldots j^1\ldots k^2\rangle}{\langle i^2\ldots j^2\ldots k^1|i^2\ldots j^2\ldots k^1\rangle}\right]^2 = \left[\frac{M_j\cdot 1}{M_k\cdot 1}\right]^2 = 1 \tag{1}$$

denotes the 1-electron transition-dipole operator, and i, j, and k are occupied π-orbital indices. We will term these Koopmans' theorem "allowed" configurations KTa, where $a = 1 + (k - j)$, j being the vacated orbital which may vary from i to k.

The essence of the distinction between the KTM and NKM can be seen most easily by retaining both the single-configuration representations and the frozen-orbital conditions as the zero-order approximation. In the most primitive version,[5b] the NKM considers the lowest ionic configuration with two-electron promotion, i.e., one electron from the HOMO (k) to the free-electron function (f) and the second from k to the LUMO (l). Such a two-particle excitation can be called "forbidden" because of the orthogonality in the electronic overlap integrands left after the moment integral ($\langle f|T|k\rangle = M_k$) has been evaluated (eq 2). We will denote this lowest Koopmans' theorem "forbidden" configuration KT_1^*.

$$A_{\psi^0\rightarrow\psi^*(i^2\ldots j^2\ldots k^0l^1f^1)} = [M_k\cdot\langle i^2\ldots j^2\ldots k^1|i^2\ldots j^2\ldots k^0l^1\rangle]^2 = M_k^2\cdot 0 = 0 \tag{2}$$

Table I. Primitive NKM Rationalization of the Lowest $^2B_{2g}$ Bands[a] in the He I PE Spectrum of 1

	areas (relative)		$^2B_{2g}(+)$ positions, eV		
basis	$^2B_{2g}(-)$	$^2B_{2g}(+)$	KTM	ΔE_{CI}	NKM
MNDO[1]	0.41	0.59	10.7	+0.7	11.4
ref 3[b]	0.31	0.69	10.5[c]	+0.4	10.9
PPP[10]	0.32	0.68			
HAM/3/CI	0.34	0.66	10.6	+0.5	11.1

[a] Using 9.7 eV as the position of the lower ($^2B_{2g}(-)$) 2 × 2 CI stationary state. [b] Using the published[3] value for a^+ and the present (over-simplified 2 × 2 CI) model. [c] Structure representation[2] value.

The NKM offers a more general picture of PES because it allows for the intensity borrowing effects which attend configuration interaction (CI) mixing of KT_1^* with the KT_a's. The theory of CI of doublets[6] imposes two conditions. One is that symmetry of a KT_a which mixes with KT_1^* must be the same as that of a KT_1^*. For even alternate polyenes this means that KT_1^* will not perturb KT_1 (the ground state for the ion in the present simple version of the model).

The second condition is that the energy of the KT_a's of appropriate symmetry must be close to that of KT_1^* (compared to the CI matrix element[7] connecting them). In the simplest case in which KT_1^* mixes with one KT_a, the 2 × 2 CI for the ion yields[7] a low-energy ionic stationary state (ψ_-^+) and a high-energy ionic stationary state (ψ_+^+) expressed as shown

$$\psi_-^+ = (a^+)KT_a - (b^+)KT_1^* \qquad \psi_+^+ = (b^+)KT_a + (a^+)KT_1^*$$

where a^+ and b^+ are the coefficients resulting from the CI linear variational procedure for the ion. The areas of the PE transitions to these two ionic states, relative to that for a pure KT_a state (such as KT_1 in the present approximation), will be[2,3]

$$\frac{A_{\psi^0\rightarrow\psi_-^+}}{A_{\psi^0\rightarrow KT_1}} = (a^+)^2 \qquad \frac{A_{\psi^0\rightarrow\psi_+^+}}{A_{\psi^0\rightarrow KT_1}} = (b^+)^2$$

Normalization indicates that $(a^+)^2 + (b^+)^2 = 1$. Thus, this primitive NKM predicts a *sharing* of one unit of PE spectral area between two ionic states, i.e., two relatively weak spectral bands above and below the position of the single band (of unit area) predicted by the KTM.

The validity of our NKM interpretation of the spectra of **1** and **2** depends on KT_1^* being energetically near KT_3 in each case. Dewar argues that KT_1^* should be ca. 12.2 eV (relative to neutral **1**). His arguments used the observed optical transition energy for neutral **1** (4.1 eV)[1,9] or the calculated (MNDO) energy gap between the HOMO and the lowest virtual orbital of **1** and $\mathbf{1}^+$ (7.6 and 7.1 eV, respectively[1]). The optical transition energy[9] for neutral **1** gives a high estimate for the $KT_1^* - KT_1$ energy difference because this observed transition contains the addition of the singlet–triplet splitting integral (+1.8 eV in HAM/3). The adjusted estimate of the energy of KT_1^* could thus be put near 10.4 eV (12.2–1.8), a little lower than that of KT_3 (as given by MNDO, 10.7 eV).[1]

Using these two estimates for the diagonals in the 2 × 2 CI (10.4 and 10.7 eV) and 9.7 eV as the final position of the lower member ($\psi_-^+ = {}^2B_{2g}(-)$) for **1**, one obtains the values for $(a^+)^2$, $(b^+)^2$, and the CI shift (ΔE) for the upper member of the 2 × 2 CI pair ($\psi_+^+ = {}^2B_{2g}(+)$) shown in the first row of Table I. They are compared with our published[3] values, those from a subsequent Pariser–Parr–Pople calculation,[10] and those of the present HAM/3-CI formalism. All of these methods agree qualitatively in predicting the third π (KTM) band in **1** should be split into

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(5) (a) Åsbrink, L.; Fridh, C.; Lindholm, E. *Chem. Phys. Lett.* **1977**, *52*, 69. Åsbrink, L.; Fridh, C.; Lindholm, E.; de Bruijn, S.; Chong, D. P. *Phys. Scr.* **1980**, *22*, 475–82. Koenig, T.; Imre, Daniel; Hoobler, James A. *J. Am. Chem. Soc.* **1979**, *101*, 6446. (b) The completion of the molecular-orbital formalism requires a linear combination of configurational functions for both the neutral precursor and the ions.

(6) Salem, L. "Molecular Orbital Theory of Conjugated Systems",; W. A. Benjamin: Reading, Mass., 1966; pp 435–443.

(7) We assume the off-diagonal CI matrix element to be positive.

(8) Our term symbols with "superscript 2" are related to the axis shown[2] by the structure labeled D_{2h} with the molecular plane taken as the yz. Dewar's term symbols[1] use xy as the molecular plane. His b_{1g} orbital at 11.76 eV is σ and not π as indicated.[1]

(9) Pearson, J. M.; Six, H. A.; Williams, D. J.; Levy, M. *J. Am. Chem. Soc.* **1971**, *93*, 5034–5040.

(10) Private communication from Josef Michl; we are grateful to Professor Michl and the Utah group for sharing this result on the doublet of **1**.

Table II. Calculated[a] and Observed[2,3] PE Band Positions (eV) and Intensities

	1 (D_{2h})		2 (C_{2h})[14]		3 (D_{2h})
HAM/3[b]	ΔE_{CI} (int.)	obsd (int.)[2]	ΔE_{CI} (int.)	obsd (int.)[3]	ΔE_{CI} (int.)
7.85 $^2B_{3u}$	7.92 (1.0)	7.87 (1.0)	7.77 (1.0)	7.58 (1.0)	9.0 (1.0)
9.51 $^2B_{1g}$	9.41 (1.0)	9.7 (1.2)	8.91 (1.0)	8.97 (0.9)	10.3 (1.0)
(10.30)[c] $^2B_{2g}$*	9.70[c] (0.4)*		9.62[c] (0.4)*	9.80 (0.5)*	10.9[c] (0.3)*
10.41 $^2B_{2g}$	11.02 (0.6)		10.78 (0.6)	10.9	12.0 (0.7)
11.58 σ	11.37 (1.0)	11.4	σ 11.09 (1.0)		12.4 (1.0)
11.92 $^2B_{3u}$	11.85 (1.0)		11.22 (1.0)		σ 13.6 (1.0)

[a] Geometries were essentially those given in ref 1 except for 3 where the C–F bond length was 1.32 Å and the two C–C bond lengths were 1.33 Å (double) and 1.48 Å (single). [b] The standard HAM/3-PES[5] calculational results. [c] KT_1*.

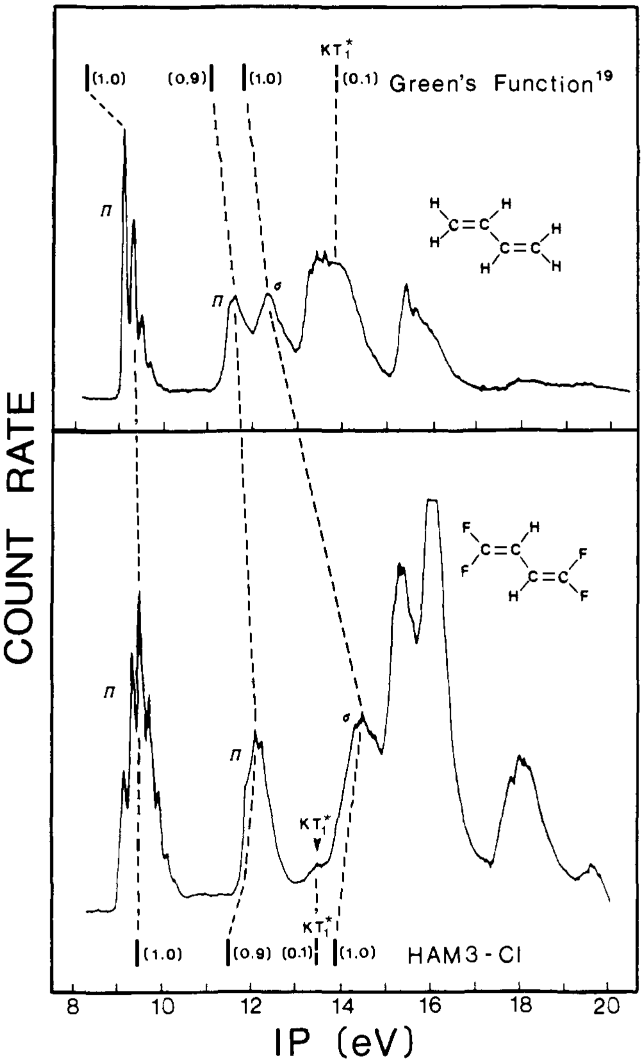

Figure 1. Calculated positions and intensities (in parenthesis) for 1,3-butadiene[19] and 1,1,4,4-tetrafluorobutadiene. Note the contribution of KT_1* for 1,3-butadiene is not resolved from the major band area assigned to the transitions to allowed α states of the same transition energy.

a weak lower member and a stronger upper member (of less than unit spectral intensity). We take strong exception to Dewar's statement[1] that our assignments "must therefore be rejected because they do not account for the low intensities of the postulated third ionizations".[11-13]

Table II shows perliminary results of a more extensive semiempirical CI model that is under development here and that is based on the HAM/3 method of Lindholm. These calculations, at present, examine the effects of the lowest 75 configurations of the ion. The results for **1** and **2** are in reasonable accord with the observations. They appear to confirm the NKM interpretation. Table II also contains the predicted spectrum of **3**. The important feature of this prediction is the division of the spectral area for KT_3 between two band maxima. The perfluoro effect[15] should raise the lowest σ ion state of **3** above all *five observable* π ionizations predicted by the NKM. The distinction between the KTM and NKM seems clear enough to allow an experimental test and we are presently exploring this possibility.

Finally, we also take exception to Dewar's statement that "no such (NKM or $I + E$) bands have been reported". Herrick[16] has recently considered the ions of linear polyenes from a purely group theoretical basis and called attention to the weak feature at 13.4 eV (Figure 1) in the experimental spectrum of 1,1,4,4-tetrafluorobutadiene.[17] His approach confirms the early conclusions of Schwieg[18] (using CI methods) and the subsequent Green's function[19] results in predicting important correlation effects on the position and intensity of the second π band in butadiene. The present HAM/3-CI method supports the notion that these effects will be almost the same for planar fluorocarbons as for their hydrocarbon analogues.

In summary, we have shown the NKM model is supported by HAM/3-CI calculations for **1** and **2**. These effects are proposed to be very similar for planar fluorocarbons and hydrocarbons. The PE spectrum of **3** is predicted in advance of its measurement. The NKM effects will probably be most evident in unstable species such as **1**–**3** but are important in other stable polyenes such as butadiene.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this work. It is also a pleasure to acknowledge the fruitful discussions on this general topic with Prof. Armin Schweig in April of 1981 and the help of our col-

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(11) Part of the basis of this statement appears to arise from confusing the intensity sharing effect described in our analysis[2,3] with the related CI effects in the optical spectrum of the ion.[12a] In the present model, the transition from the electronic ground state of the ion (KT_1) to $^2B_{2g}(-)$ would be much weaker than that to $^2B_{2g}(+)$ because of the partial cancellation of two similar transition moments associated with the negative sign. The optical transitions from KT_1 to KT_3 and KT_1* are both single-particle excitations which distinguishes the optical spectrum case from the PE spectrum case. This distinction was lost in Dewar's account.

(12) (a) A very similar model has been used in the analysis of the optical spectra of radical cations.[12b] (b) Forster, P.; Gswind, R.; Haselbach, E.; Klemm, U.; Wirz, J. *Nouv. J. Chim.* **1980**, *4*, 365. Haselbach, E.; Klemm, U.; Buser, U.; Gswind, R.; Jungen, M.; Kloster-Jensen, E.; Maier, J.; Marthaler, O.; Christen, H.; Baertschi, P. *Helv. Chim. Acta* **1981**, *64*, 823–834.

(13) (a) Dēwar seems to suggest that the weak band at 9.8 eV in the published[3] spectrum of **2** is due to contamination by the related 2,4,5-trimethylbenzyl radical. Purity of the furnace effluent is of constant concern in this work which is why our equipment[13b] was designed to allow product studies. For **1** the expected[9] polymer was identified by infrared comparison. (b) Imre, Daniel; Koenig, T. *Chem. Phys. Lett.* **1980**, *73*, 62.

(14) The symmetry and term symbols for **2** in ref 1 are scrambled. Those of Table I of ref 1 are apparently derived from the incorrect C_{2v} point group though the correct C_{2h} point group is mentioned with the table. However, C_2 symmetry is indicated by the (partial) structure for **2**.

(15) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1457. Brundle, C. R.; Robin, M. B.; Kuebler, N. A. *Ibid.* **1972**, *94*, 1466.

(16) Herrick, David R. *J. Chem. Phys.* **1981**, *74*, 1239–1255.

(17) Brundle, C. R.; Robin, M. B. *J. Am. Chem. Soc.* **1970**, *92*, 5550.

(18) Lauer, G.; Schulte, K.; Schweig, A. *Chem. Phys. Lett.* **1975**, *32*, No. 1, 163.

(19) Von Niessen, W.; Bieri, G.; Schirmer, J.; Cederbaum, L. S. *Chem. Phys.* **1982**, *65*, 157–76 and references therein. Cederbaum, L. S.; Domcke, W.; Schirmer, J. *J. Chem. Phys.* **1978**, *69*, 1591.

leagues Prof. David Herrick and Prof. Paul Engelking along with the instigating influence of William T. Simpson.

Note in Added Proof: Since the submission of this manuscript Prof. Schweig has informed us of additional MO-CI results that are consistent with an NKM interpretation of the spectra of **1** and **2** as well as a number of other related systems. He also reminded us of his first private communication of the calculated CI effect in $\mathbf{1}^+$ in April of 1981. The publication of these results should appear shortly.

Registry No. 1, 502-86-3; **2**, 63238-49-3; **3**, 84694-70-2; 1,1,4,4-tetrafluorobutadiene, 407-70-5.

Electronegativity and Bond Energy

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Abstract: Recognition of quantitative relationships among atomic structure, electronegativity, nonpolar covalent radius, and homonuclear bond energy has permitted a complete revision of electronegativities of all major group elements and a more accurate evaluation of their radii and homonuclear bond energies. The new values have been tested by application to calculating the bond energies in practically all binary compounds of major group elements with halogen, oxygen, sulfur, and positive hydrogen and many other inorganic compounds having more than one kind of bond per molecule. In agreement with the quantitative theory of polar covalence, the calculated energies agree with experimental values within probable limits of experimental error for most of the 304 compounds studied.

Electronegativities of all the active major group elements, including zinc, cadmium, and mercury, have been completely revised on the basis of a study of the interrelationships among atomic structure, nonpolar covalent radius, electronegativity, and homonuclear covalent bond energy. The revised values have been thoroughly tested by application to the calculation of bond energies in more than 300 inorganic compounds containing about 400 kinds of bonds. These compounds, both nonmolecular solids and gaseous molecules, include nearly all of the binary compounds of positive hydrogen, binary halides, oxides, and sulfides of the major group elements for which adequate experimental data are available.[1-7] Also included are 85 compounds each consisting of more than one kind of bond: mixed halides, oxyhalides, hydroxy acids, and a wide variety of miscellaneous compounds. Agreement between calculated and experimental bond energy for most of these compounds is on the average within probable experimental error. Greater differences found for 15% of the compounds studied are believed to result most probably from experimental error in determination of the heats of formation. This paper presents (Table I) the new electronegativity values, together with revised nonpolar covalent radii, homonuclear bond energies, and the electronegativity changes corresponding to the acquisition of unit charge. It also describes the details of revision and discusses the interrelationships among fundamental atomic properties.

Polar Covalence. The quantitative theory of polar covalence has been presented in detail elsewhere.[8-11] It will be reviewed very briefly here to emphasize an important aspect of the validity of this work. A polar covalent bond is treated as a blend of the two extremes, nonpolar covalence and complete ionicity. The energy of the nonpolar covalent form, E_c, is simply the geometric mean of the two homonuclear covalent bond energies, corrected for any difference between the actual bond length, R_0, and the

Table I. Electronegativities, Covalent Radii, and Homonuclear Bond Energies

element	S	ΔS_i	r_c	E'''	E''	E'
H	2.592	2.528	32.0	104.2		
Li	0.670	1.285	133.6	24.6		
Be	1.810	2.112	88.7	67.6		
B	2.275	2.368	82.2	76.7		
C	2.746	2.602	77.2	85.4		
N	3.194	2.806	73.4	94.9	66.9	38.8
O	3.654	3.001	70.2	104.0	68.8	33.6
F	4.000	3.140	68.1	113.1	76.8	40.5
Na	0.560	1.175	153.9	16.4		
Mg	1.318	1.802	137.3	42.3		
Al	1.714	2.055	125.8	48.2		
Si	2.138	2.296	116.9	54.1		
P	2.515	2.490	110.7	60.0	56.9	53.7
S	2.957	2.700	104.9	65.9	60.4	54.9
Cl	3.475	2.927	99.4	71.8	64.9	58.0
K	0.445	1.047	196.2	13.1		
Ca	0.946	1.527	174	30.8		
Cu	2.033	2.239	133.1	31.3		
Zn	2.223	2.341	129.2	35.8		
Ga	2.419	2.442	125.6	40.3		
Ge	2.618	2.540	122.3	44.8		
As	2.816	2.635	119.4	49.3	45.1	40.9
Se	3.014	2.726	116.7	53.8	46.0	38.2
Br	3.219	2.817	114.2	58.3	52.2	46.1
Rb	0.312	0.877	216	12.4		
Sr	0.721	1.333	191	24.6		
Ag	1.826	2.122	153.3	27.7		
Cd	1.978	2.208	149.3	30.4		
In	2.138	2.296	145.5	33.1		
Sn	2.298	2.380	142.0	35.8		
Sn(II)	1.477	1.908	142.0	35.8		
Sb	2.458	2.461	138.9	38.5	35.8	33.0
Te	2.618	2.540	136.0	41.2	39.2	37.2
I	2.778	2.617	133.3	43.9	40.0	36.1
Cs	0.220	0.736	235	10.8		
Ba	0.651	1.267	198	22.2		
Hg	2.195	2.326	150.0	8.6		
Tl	2.246	2.353	149.0	16.6		
Tl(I)	0.987	1.560	149	16.6		
Pb	2.291	2.376	148	24.2		
Pb(II)	1.900	2.164	148	24.2		
Bi	2.342	2.403	147	32.2		

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