

A simple interpretation of the Fe_2^- photoelectron spectrum

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The photoelectron spectrum of Fe_2^- can be simply interpreted in terms of electron detachment from the mildly antibonding $4s\sigma_u^*$ orbital of a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ anion. This interpretation implies a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ configuration for the ground state of Fe_2^- , correlating with one ground state ($4s^23d^6$) and one excited state ($4s^13d^7$) Fe atom. A comparison of the bond length and vibrational frequency of Fe_2 to values for transition metal dimers containing single $4s-4s$ bonds is suggestive of $3d-3d$ bonding in this molecule. The results of preliminary full-valence configuration interaction calculations provide strong support for the proposed Fe_2 and Fe_2^- configurations.

I. INTRODUCTION

A recent report of the photoelectron spectrum¹ of Fe_2^- contrasted these results with *ab initio* predictions² of a $4s-4s$ singly bonded Fe_2 ground state arising from the interaction of two $4s^13d^7$ excited state atoms. The experimental data were shown to be incompatible with this picture, but an alternative model capable of satisfactorily explaining the spectrum remained elusive. Subsequently, photoelectron data^{3,4} for Cu_2^- and Ni_2^- , as well as careful theoretical investigations⁵ of the electronic structure of Cu_2^- , have become available. In light of these results, we propose here a new qualitative model for the ground states of Fe_2 and Fe_2^- , one which affords a simple interpretation of the previously puzzling photoelectron spectrum.

II. REVIEW OF EXPERIMENTAL RESULTS

The photoelectron spectrum of Fe_2^- , reproduced in Fig. 1, shows just two vibronic band systems throughout the region probed by the 488 nm (2.540 eV) photodetachment laser. The bands at lower electron binding energy were assigned¹ to the transition between the electronic ground states of Fe_2^- and Fe_2 ; this assignment is discussed further below. The data show that the ground state of Fe_2^- has a vibrational frequency of $250 \pm 20 \text{ cm}^{-1}$, a bond length of $2.10 \pm 0.04 \text{ \AA}$, and a bond strength of $1.53 \pm 0.17 \text{ eV}$ (assuming values^{2,6} of $2.02 \pm 0.02 \text{ \AA}$ and $0.78 \pm 0.17 \text{ eV}$ for Fe_2). These results are indicative of a strong chemical bond in the anion. The second band system, $0.534 \pm 0.004 \text{ eV}$ higher in energy, was assigned to a transition from the ground state of the anion to an excited electronic state of Fe_2 . Peak separations and relative intensities in both systems indicate the same vibrational frequency and bond length for the two observed Fe_2 states, within experimental error.

III. DISCUSSION

The photoelectron spectra of Cu_2^- , Ni_2^- and of the first-row atomic transition metal anions⁷ are all dominated by $4s$ rather than $3d$ electron detachment, strongly suggesting that the two band systems observed in the Fe_2^- spectrum are also due to detachment from $4s$ -like molecular orbitals. In view of the strongly bonding⁸ $4s\sigma_g$ orbital in Ni_2 and Cu_2 , and the similar vibrational frequencies and bond lengths of Fe_2 ,^{6,9} Ni_2 ,^{4,10} and Cu_2 ,^{11,12} it is likely that the $4s\sigma_g$ orbital in Fe_2 is also strongly bonding. Therefore, the virtually identical bond lengths and vibrational frequencies in the two observed states of Fe_2 suggest that they both have the same $4s\sigma_g$ occupation.

This restriction leaves a limited number of possibilities.

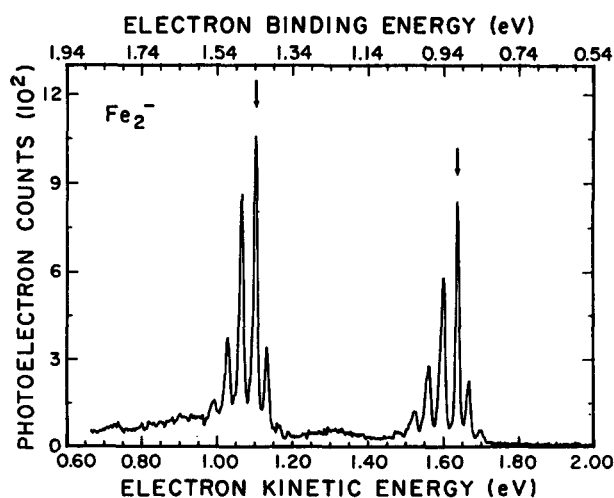


FIG. 1. $\text{Fe}_2^- \rightarrow \text{Fe}_2 + e^-$ photoelectron spectrum at 488 nm (2.540 eV). Arrows mark origins of the two observed vibronic band systems. The weak, broad band between these is due to a small amount of $\text{Fe}(\text{CO})_2^-$ impurity in the 112 amu ion beam. Reprinted from Ref. 1.

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We first consider a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{14}$ configuration for Fe₂⁻, in analogy with the Cu₂⁻ case.^{3,5} The two 4s-detachment processes of lowest energy would then produce the neutral molecule in $(4s\sigma_g)^2(3d)^{14}$ and $(4s\sigma_g)^1(4s\sigma_u^*)^1(3d)^{14}$ states, which differ in their 4s_g orbital occupancies. On the other hand, a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ configuration for Fe₂⁻, correlating with ground state Fe ($4s^23d^6$) and ground state Fe⁻ ($4s^23d^7$), would fulfill the necessary criterion. Detachment of either 4s_u^{*} electron would produce two $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ Fe₂ states with the 4s_u^{*} electron high- or low-spin coupled to the $(3d)^{13}$ "core." These states would undoubtedly display very similar vibrational frequencies and bond lengths, as is observed. The 0.53 eV separation between the two Fe₂ band systems is actually very similar to the 0.61 eV (*M_J*-averaged) splitting¹³ between the ³F and ⁵F states of the Fe atom in its $3d^7(4F)4s^1$ configuration.

As noted above, the vibrational frequency, bond length, and bond dissociation energy obtained from the photoelectron spectrum indicate that the Fe₂⁻ anion has a strong chemical bond. This conclusion would at first appear to preclude a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ occupation, in which the four 4s-derived electrons make no formal bonding contribution. However, a closer inspection of the 4s_u^{*} orbital in the anion indicates that the proposed configuration is in fact consistent with these data. Recent extensive *ab initio* calculations⁵ of Cu₂⁻ reproduce well the observed changes in bonding on electron attachment, and show that the 4s_u^{*} orbital is extensively polarized with little electron density in the internuclear region. Thus, although the 4s_g orbital is strongly bonding as expected, the antibonding character of the 4s_u^{*} orbital is greatly reduced by 4s σ -4p σ mixing. In the neutral metal dimers, on the other hand, this orbital is expected to be less diffuse and more antibonding. In the Mn₂ ground state, the analogous $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{10}$ configuration yields only a weak, van der Waals bond.¹⁴

These arguments support the view that Fe₂⁻ has a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{13}$ ground state configuration, and thus that the two Fe₂ states observed in the photoelectron spectrum have $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ occupations. The 0–1 and 0–2 vibrational intervals of these Fe₂ states both agree with those reported⁹ for the ground electronic state to within the uncertainty of the photoelectron experiment (15 cm⁻¹). This agreement indicates that the potential energy surfaces of both states are very similar to that of the ground state. In view of the strongly bonding character of the 4s_g orbital and the somewhat antibonding 4s_u^{*} orbital expected in the neutral molecule, such a close resemblance is highly unlikely for states with different 4s_g or 4s_u^{*} occupations. The 0–1 vibrational intervals of all of the first-row metal dimers investigated to date^{1,3,4} decrease by ≈ 50 cm⁻¹ on addition of an electron to the 4s_u^{*} orbital, and the A ← X transition of Cu₂, which may be due to a 4s_u^{*} ← 3d excitation, is accompanied by a vibrational frequency decrease of 74 cm⁻¹.¹⁵

These considerations indicate that the *ground* state of Fe₂ also has a $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ configuration, presumably with the 4s_u^{*} electron high-spin coupled to maximize exchange interactions. This configuration clearly will give rise to a large number of electronic states with different

couplings of electrons within the $(3d)^{13}$ core, and it is likely that many of these states will exhibit similar vibrational frequencies. Consequently, it cannot be inferred from the vibrational data alone that the lowest energy Fe₂ state observed in the photoelectron spectrum is the ground state. In fact, the propensity for single electron photoelectron processes (i.e., detachment with no additional electron reorganization) would favor transitions to states with the same 3d-shell configuration as in the ground state of Fe₂⁻, which may well differ from that of Fe₂. However, previous experience in the photoelectron spectroscopy of negative ions, as well as neutral species, indicates that it is likely that the ground state transition would be detectable in a complex system such as Fe₂ due to electron correlation effects. These considerations strongly favor the assignment of the bands at lower electron binding energy to the ground state transition; however, this assignment is not critical to the central argument of this paper.

The proposed $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{13}$ Fe₂ configuration corresponds to one ground state ($4s^23d^6$) and one excited ($4s^13d^7$) Fe atom at dissociation, and to an admixture of the $4s^23d^6$ and $4s^13d^7$ occupations for each Fe atom at finite separation. This molecular configuration is supported by a comparison of the ground state configurations of the first-row homonuclear metal dimers to their respective $4s^23d^m \rightarrow 4s^13d^{m+1}$ atomic promotion energies. At one extreme, the very large promotion energy of Mn (2.14 eV) results in a $(4s\sigma_g)^2(4s\sigma_u^*)^2(3d)^{10}$ ground state configuration for Mn₂ correlating to the $4s^23d^5 + 4s^23d^5$ atomic limit.¹⁴ In contrast, the $(4s\sigma_g)^2(3d)^{2m+2}$ ground state configuration is observed⁸ for the dimers of V, Cr, Ni, and Cu, which have $4s^13d^{m+1}$ atomic ground states or very small (≤ 0.25 eV) promotion energies. The intermediate promotion energies¹³ of Sc (1.43) and Ti (0.81 eV) favor the $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{2m+1}$ configuration, which correlates asymptotically to the mixed $4s^23d^m + 4s^13d^{m+1}$ atomic limit. This configuration has in fact been demonstrated for the $^5\Sigma_u^-$ ground state^{16–20} of Sc₂ and has been calculated^{17,20} to give rise to the ground state of Ti₂. In view of the similar $4s^23d^6 \rightarrow 4s^13d^7$ atomic promotion energy of Fe (0.87 eV),¹³ it appears quite reasonable that the ground state of Fe₂ should also derive from this mixed asymptote. Consistent with this view, the analogous $\sigma^2\sigma^*1d^6$ configuration of FeH produces an excited electronic state only 0.24 eV above the σ^2d^7 ground state.²¹ The atomic promotion energy of Co (0.42 eV), and the similarities between the Fe₂⁻ and Co₂⁻ photoelectron spectra,¹ also suggest that the $(4s\sigma_g)^2(4s\sigma_u^*)^1(3d)^{15}$ configuration is a reasonable candidate for the ground state of Co₂.

The proposed Fe₂ configuration is also consistent with its lower ionization potential (6.30 ± 0.01 eV)²² than that of Cu₂ (7.894 ± 0.015 eV)²³ or Ni₂ (7.1 ± 0.7 eV),^{8,10} since in the latter two cases a 4s_g rather than a 4s_u^{*} electron must be detached. Furthermore, the photoionization spectrum of Fe₂ shows a sharp threshold to the 0–0 transition.²² This result is difficult to reconcile with detachment of a strongly bonding 4s_g electron from the commonly assumed $(4s\sigma_g)^2(3d)^{14}$ ground state configuration, but is understandable in

terms of the detachment of an only mildly antibonding $4s\sigma_u^*$ electron from a $(4s\sigma_g)^2 (4s\sigma_u^*)^1 (3d)^{13}$ molecule. The ground state configurations proposed here are also compatible with the surprising observation that the bond strength of Fe₂⁻ (1.53 ± 0.17 eV)^{1,3} is almost twice that of Fe₂ (0.78 ± 0.17 eV),² despite relatively modest changes in the vibrational frequency and bond length on electron attachment. To form Fe₂ in a $(4s\sigma_g)^2 (4s\sigma_u^*)^1 (3d)^{13}$ state one atom must be promoted to $4s^1 3d^7$, whereas a $(4s\sigma_g)^2 (4s\sigma_u^*)^2 (3d)^{13}$ anion can be formed from the ground states of Fe and Fe⁻. Thus, the anion bond energy would be expected to exceed that of the neutral molecule by approximately the atomic promotion energy (0.87 eV), even if the potential energy surface near equilibrium were to remain largely unchanged on electron attachment to the $4s\sigma_u^*$ orbital.

The important issue of the extent of $3d$ - $3d$ bonding in Fe₂ can be addressed in light of these results. A $(4s\sigma_g)^2 (4s\sigma_u^*)^1 (3d)^{13}$ configuration would imply a formal bond order of only one-half for the $4s$ - $4s$ bond in Fe₂. In contrast, both Ni₂ and Cu₂ are reported to have a $(4s\sigma_g)^2 (3d)^{2m+2}$ ground state with a single $4s$ - $4s$ bond and a nonbonding $3d$ core.^{8,10} Nevertheless, the bond length of Fe₂ (2.02 ± 0.02 Å)⁶ is shorter than that of either Ni₂ (2.200 ± 0.007 Å)¹⁰ or Cu₂ (2.2197 Å).¹¹ In addition, the Fe₂ vibrational frequency (300 cm⁻¹)⁹ is comparable to that recently observed⁴ for Ni₂, and actually exceeds the Cu₂ value (266.43 cm⁻¹).¹¹ These comparisons corroborate the earlier conclusion¹ that the $3d$ electrons participate in the Fe₂ bond. A strengthened interaction between $3d$ orbitals over that predicted by previous *ab initio* calculations² would have the additional effect of reducing the density of electronic states in the spectral region probed in this experiment. The occurrence of $3d$ - $3d$ bonding in Fe₂ (and, presumably, in Fe₂⁻ as well) may account at least in part for the surprisingly sparse appearance of the photoelectron spectrum and for the absence of detectable transitions from electronically excited anions.

IV. CALCULATIONS

To further assess the proposed assignment scheme, quantum mechanical calculations were performed. The electronic structure of the suggested states is obviously quite complicated. Walsh²⁴ has observed spontaneous symmetry breaking when d^{13} occupations for Fe₂ are treated without imposing inversion symmetry, which indicates substantial correlation effects in the d space. More recent studies by Bauschlicher²⁵ confirm that the inclusion of substantial dynamical correlation is required to describe the binding in these systems adequately. However, given that present calculations compare systems with the same d occupations (and, indeed, the same d spin and spatial coupling) at essentially the same bond lengths, it should still be possible to arrive at semiquantitative results without accounting for these effects.

We have performed full-valence configuration interaction calculations for $4s\sigma_u^*$ electron detachment from a

$(4s\sigma_g)^2 (4s\sigma_u^*)^2 (3d)^{13}$ Fe₂⁻ anion. At each bond length studied, a CASSCF calculation was performed on Fe₂⁻, including four electrons in the two $4s$ -derived MOs and all possible distributions of 13 electrons in the ten $3d$ -derived MOs. Several different $(3d)^{13}$ occupancies, each with maximum spin $S = 7/2$, were considered. Full valence CI calculations were then performed on states with one electron removed from the $4s\sigma_u^*$ orbital, selecting those CI roots whose $(3d)^{13}$ occupancy matched that of the ion calculation. For example, to model detachment from the ${}^8\Phi_g^-$ Fe₂⁻ state, the appropriate ${}^9\Phi_u$ and ${}^7\Phi_u$ states of Fe₂ were used. The choice of a high-spin state for Fe₂⁻ is reasonable but arbitrary, and the results presented here should *not* be interpreted as arguments for high-spin ground states of Fe₂⁻ or Fe₂. The procedure used is analogous to the use of Koopmans' theorem for single determinant wave functions, but it allows for relaxation effects and recouplings in the $3d$ shell. Bond lengths and harmonic frequencies were obtained from quadratic fits in $1/r$ to energies calculated at three bond lengths. All calculations were performed using the MOLECULE-SWEDEN²⁶ codes on the CRAY X-MP/48 at NASA-Ames.

The basis set used in these calculations was derived from Wachters ($1s$ $9p$ $5d$) primitive set,²⁷ with the outermost two s -type primitives replaced with four (exponents 0.26, 0.08, 0.03, 0.012). The set was further augmented with three p -type primitives (exponents 0.202 37, 0.062 76, 0.025) and two d -type primitives (exponents 0.1133 and 0.044). With the resulting ($16s$ $12p$ $7d$) uncontracted set a CI calculation on Fe⁻ was performed, including all single and double excitations from a single reference configuration and correlating the valence electrons only. The basis was then contracted to [$6s$ $5p$ $3d$] using the most strongly occupied natural orbitals from the CI calculation as basis functions.²⁸ The resulting basis is effectively of triple zeta quality in the valence.

For all of the cases examined [$(3d)^{13}$ core configurations ${}^8\Phi_g^-$, ${}^8\Delta_g^-$, and ${}^8\Sigma_g^-$] the high- and low-spin states of the neutral molecule were found to be split by about 0.32 eV, 0.13 eV lower than the calculated atomic 5F - 3F splitting of 0.45 eV. Similarly, the experimentally observed molecular splitting (0.53 eV) is 0.08 eV lower than the known 0.61 eV (M_j -averaged) splitting for the Fe atom in the $3d^7 4s^1$ configuration. The calculated bond lengths (2.16 Å) and vibrational frequencies (323 - 327 cm⁻¹) of these states are virtually identical (experimental: 2.02 Å, 300 cm⁻¹). The calculated vibrational frequency, as well as the frequency reduction (35 - 40 cm⁻¹) and bond elongation (0.04 Å) on addition of the second $4s\sigma_u^*$ electron, are also in agreement with the experimental results ($\Delta\nu = 50 \pm 20$ cm⁻¹, $\Delta r = 0.08 \pm 0.02$ Å). Thus, these calculations provide strong support for the proposed ground state configurations of Fe₂ and Fe₂⁻.

V. CONCLUSION

We have proposed a simple interpretation of the Fe₂⁻ photoelectron spectrum based on detachment of $4s\sigma_u^*$ electrons from a $(4s\sigma_g)^2 (4s\sigma_u^*)^2 (3d)^{13}$ anion. This interpretation implies a $(4s\sigma_g)^2 (4s\sigma_u^*)^1 (3d)^{13}$ ground state configuration for Fe₂, rather than the $(4s\sigma_g)^2 (3d)^{14}$ configuration that has generally been assumed. The former configuration

correlates to an admixture of the $4s^23d^6$ and $4s^13d^7$ occupations for each atom at finite separation, an admixture that is also important in describing the bonding in FeH and related metal hydrides.²⁹ The proposed Fe₂ configuration gives a formal $4s-4s$ bond order of only one-half. A comparison of its bond length and vibrational frequency to those of related metal dimers containing single $4s-4s$ bonds then indicates some additional $3d$ contribution to the bonding in Fe₂. The results of preliminary valence CI calculations provide strong support for the proposed Fe₂ and Fe₂⁻ configurations. The arguments presented here suggest that states arising from the mixed $4s^23d^m + 4s^13d^{m+1}$ atomic asymptote be more carefully considered in future theoretical investigations of Fe₂ and Co₂.

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¹D. G. Leopold and W. C. Lineberger, *J. Chem. Phys.* **85**, 51 (1986).

²I. Shim and K. A. Gingerich, *J. Chem. Phys.* **77**, 2490 (1982).

³D. G. Leopold, J. Ho, and W. C. Lineberger, *J. Chem. Phys.* **86**, 1715 (1987).

⁴K. M. Ervin, J. Ho, and W. C. Lineberger (unpublished results).

⁵(a) C. W. Bauschlicher, Jr., S. R. Langhoff, and P. R. Taylor, *J. Chem. Phys.* **88**, 1041 (1988); (b) H. Sable and S. V. O'Neil (to be published).

⁶H. Purdum, P. A. Montano, G. K. Shenoy, and T. Morrison, *Phys. Rev. B* **25**, 4412 (1982).

⁷H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985), and references therein.

⁸M. D. Morse, *Chem. Rev.* **86**, 1049 (1986), and references therein.

⁹M. Moskovits and D. P. DiLella, *J. Chem. Phys.* **73**, 4917 (1980).

¹⁰M. D. Morse, G. P. Hansen, P. R. R. Langridge-Smith, L.-S. Zheng, M. E. Geusic, D. L. Michalopoulos, and R. E. Smalley, *J. Chem. Phys.* **80**, 5400 (1984).

¹¹K. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV* (Van Nostrand, New York, 1979).

¹²K. Hilpert, *Ber. Bunsenges. Phys. Chem.* **83**, 161 (1979).

¹³C. E. Moore, *Natl. Bur. Stand. Circ. (U.S.)* **467** (1952).

¹⁴C. A. Baumann, R. J. Van Zee, S. V. Bhat, and W. Weltner, Jr., *J. Chem. Phys.* **78**, 190 (1983); J.-C. Rivoal, J. Shkhs Emampour, K. J. Zeringue, and M. Vala, *Chem. Phys. Lett.* **92**, 313 (1982).

¹⁵N. Åslund, R. F. Barrow, W. G. Richards, and D. N. Travis, *Ark. Fys.* **30**, 171 (1965); J. Lochet, *J. Phys. B* **11**, L55 (1978).

¹⁶L. B. Knight, Jr., R. J. Van Zee, and W. Weltner, Jr., *Chem. Phys. Lett.* **94**, 296 (1983).

¹⁷J. Harris and R. O. Jones, *J. Chem. Phys.* **70**, 830 (1979).

¹⁸C. Wood, M. Doran, I. H. Hillier, and M. F. Guest, *Faraday Symp.* **14**, 159 (1980).

¹⁹S. P. Walch and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **79**, 3590 (1983).

²⁰S. P. Walch and C. W. Bauschlicher, Jr., in *Comparison of Ab Initio Quantum Chemistry with Experiment*, edited by R. J. Bartlett (Reidel, Dordrecht, 1985), p. 17.

²¹A. E. Stevens, C. S. Feigerle, and W. C. Lineberger, *J. Chem. Phys.* **78**, 5420 (1983).

²²E. A. Rohlfing, D. M. Cox, A. Kaldor, and K. H. Johnson, *J. Chem. Phys.* **81**, 3846 (1984).

²³D. E. Powers, S. G. Hansen, M. E. Geusic, D. L. Michalopoulos, and R. E. Smalley, *J. Chem. Phys.* **78**, 2866 (1983).

²⁴S. P. Walch (private communication).

²⁵C. W. Bauschlicher, Jr. (private communication).

²⁶MOLECULE-SWEDEN is a vectorized SCF-MCSCF-direct CI-conventional CI-CPF-MCPF program, written by P. E. M. Siegbahn, C. W. Bauschlicher, Jr., B. Roos, P. R. Taylor, A. Heiberg, J. Almlöf, S. R. Langhoff, and D. P. Chong.

²⁷A. J. H. Wachters, *J. Chem. Phys.* **52**, 1033 (1970).

²⁸J. Almlöf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).

²⁹S. P. Walch and C. W. Bauschlicher, Jr., *J. Chem. Phys.* **78**, 4597 (1983); S. P. Walch, C. W. Bauschlicher, Jr., and S. R. Langhoff, *ibid.* **83**, 5351 (1985); D. P. Chong, S. R. Langhoff, C. W. Bauschlicher, Jr., S. P. Walch, and H. Partridge, *ibid.* **85**, 2850 (1986).