Redox Properties of the Diatomic Bare Iron Chalcogenides FeO and FeS in the Gas Phase

Jeremy N. Harvey, Christoph Heinemann, Andreas Fiedler, Detlef Schröder, and Helmut Schwarz*

Dedicated to Professor Helmut Baumgärtel on the occasion of his 60th birthday

Abstract: The electron-transfer behavior of the binary iron chalcogenides FeO and FeS has been examined by means of mass spectrometry and ab initio calculations using the averaged coupled-pair functional (ACPF) method. The experimental and theoretical results are in good agreement with each other and also with previous studies. The ionization energies (IE) of the diatomic species are found to be IE(FeO) = 8.8 ± 0.2 eV, IE(FeO^+) = 17.9 ± 0.4 eV, IE(FeS) = 8.3 ± 0.3 eV, and IE(FeS^+) = 16.3 ± 0.5 eV. Two new diatomic dications, FeS^{2+} and FeO^{2+}, are shown to exist as metastable minima on the corresponding potential-energy surfaces. The data enable an evaluation of the intrinsic gas-phase redox properties of FeS and FeO, and the comparison demonstrates that iron sulfide is more prone to undergo facile reduction and oxidation than iron oxide.

Keywords
ab initio calculations · iron oxide · iron sulfide · mass spectrometry

Introduction

Iron is one of the most abundant elements in the earth's crust, present in large amounts as its oxide and its sulfide. Hence, it is not surprising that iron is also present in many biological systems, often combined with oxygen or sulfur, and there is even some speculation that iron sulfides may have played a role in the origin of life.[1] The particular interest in the redox properties of iron chalcogenides is due to the large number of proteins that contain small iron chalcogenide clusters as redox-active centers in electron-transfer processes, such as the Fe_4S_4 core of the ferredoxins.[2] Here, we report a combined mass-spectrometric and ab initio study of the gas-phase redox properties of the diatomic FeS system, which we compare to the analogous FeO.

Experimental and Theoretical Procedures

Experiments were mostly performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described previously [3]. FeS^+ was generated by chemical ionization (CI) of a mixture of $Fe(CO)_5$ and ethylene sulfide with carbon monoxide as supporting CI gas. Under these conditions, FeS^+ is always accompanied by small amounts of FeO_2^+ owing to air leakage into the ion source [4]. The mass difference between these ions was too small to be resolved, instead the FeS^+ spectrum was corrected for interferent FeO_2^+ on the basis of the abundance of the FeO^+ fragment. As described previously [5], FeO^+ was generated by CI of $Fe(CO)_5$ with N_2O as CI gas. FeS^- was generated by negative-ion CI of $Fe(CO)_5$ by using a mixture of N_2O and CS_2 as CI gases, and FeO^- was formed by CI of a mixture of $Fe(CO)_5$ with O_2.

The energy losses associated with the electron abstraction processes, i.e., energy-resolved charge-reversal [6] ($M^- \rightarrow M^+$) and charge-stripping mass spectrometry [7] ($M^+ \rightarrow M^{2+}$), were determined by using the first two sectors, owing to the higher energy resolution of E(1) compared to E(2). To this end, the ions were mass-selected in B(1), collided with oxygen (60% transmission, *T*) in the field-free region preceding E(1), and the resulting species were recorded by scanning E(1) with energy resolutions $E/\Delta E > 2000$. The high-energy onsets of the signals were then compared with each other and converted to absolute energy differences. In both experiments, the energy necessary to remove electrons from the fast-moving projectiles is taken from their kinetic energy and leads to a shift of the signals from the expected to slightly lower values; these energy differences are referred to as ΔE and Q_{min}, respectively. For calibration of the energy scales, the well-known processes $CS_2^{\cdot -} \rightarrow CS_2^{\cdot +}$ ($\Delta E = 10.6 \pm 0.1$ eV [8]) and $C_7H_8^{\cdot +} \rightarrow C_7H_8^{2+}$ ($Q_{min} = 15.7$ eV [7]) were used. In the former experiment an additive correction was applied to compensate for the different energies of anionic and cationic species. In the latter case, where ratios of energies are measured for ions of the same polarity, the multiplicative correction method [7] was chosen; further, the Q_{min} values were also determined by using $E(2)$ for energy analysis [9]. All energy differences reported are averages of at least five independent experiments [10].

For neutralization–reionization (NR) experiments [11], FeO^+ or FeS^+ cations were mass-selected in B(1)/E(1) and collided with Xe (80% *T*). Subsequently, the remaining ions were removed from the beam by a deflector plate, the beam of neutral species was reionized by collision with oxygen (80% *T*), and the resulting cations were mass-analyzed in B(2).

Additional experiments were carried out on a Spectrospin CMS 47X FTICR mass spectrometer, which has been described in detail elsewhere [12]. FeS^+ cations were generated in the external source by laser desorption/laser ionization [13] of a compressed mixture of elemental iron and sulfur (ca. 2:1); a similar procedure has been described in the literature [14]. By a system of electric potentials and lenses the so-formed cations were transferred to the analyzer cell, which is located within a superconducting magnet (max. field strength 7.05 Tesla). Subsequently, FeS^+ cations were mass-selected by using the FERETS technique [15], a computer controlled ion-ejection protocol that combines single-frequency pulses with frequency sweeps to optimize ion isolation. Owing to the injection of the ions from the external ion source, the mass-selected ions exhibit an excess of kinetic energy compared to thermal motion, and the laser desorption process may also lead to excited species. In order to afford thermalization of FeS^+, argon was pulsed in several times (ca. 200 collisions) and pumped off prior to reactivity measurements. Reagent gases were introduced to the FTICR cell either via leak or pulsed valves. All data were accumulated and processed on-line by means of an ASPECT 3000 minicomputer.

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Ab initio MO calculations for FeS^+ and FeS^{2+} were carried out with the MOLPRO96 program [16] on the CRAY-J932/16-8192 computer at the Konrad-Zuse-Zentrum für Informationstechnik Berlin. Total energies were computed at the averaged coupled-pair functional (ACPF) [17] level of theory, starting from the corresponding complete active space self-consistent field (CASSCF) wave functions [18]. Only the valence (Fe: 3d and 4s; S: 3s and 3p) electrons were correlated. Unless specified otherwise, the ANO basis sets (BS I) used were (21s 15p 10d 6f 4g)/[8s 7p 6d 4f 2g] for iron [19], and (17s 12p 5d 4f)/[7s 6p 4d 3f] for sulfur [20]. Additional calculations were performed with an enlarged basis set (BS II), including an additional h function for iron (exponent 2.0) and two additional g functions for sulfur (exponents 0.463 and 1.071). Geometry optimizations were performed in a stepwise manner by variation of the Fe–S distances, and anharmonic frequencies were derived from a spline fit through the calculated potential curves. If not specified otherwise, all auxiliary thermochemical data and state-averaged atomic energies were taken from ref. [8].

Results

We will first present the experimental and theoretical results obtained for the electron affinities (EAs) and the first and second ionization energies (IEs) of FeO and FeS. Then, these findings will be discussed in the context of the redox properties of the two binary iron chalcogenides.

Experimental results: The electron affinity (EA(FeS) = 1.7 ± 0.1 eV)[21] and the ionization energy of neutral FeS have been reported in the literature.[22] The IE(FeS), reported as 8.7 ± 0.4 eV, was, however, derived by a thermodynamic cycle[22] from the bond-dissociation energy (D_0) of FeS^+ and depends on the heat of formation (ΔH_f°) of molecular FeS in the gas phase, a value that may be somewhat imprecise owing to extrapolation from older high-temperature studies.[23] Thus, we followed two different ways to determine IE(FeS) more directly.

First, we measured the sum of the EA and the IE of neutral FeS by energy-resolved charge reversal (CR) mass spectroscopy of FeS^-. The anion was produced as described above, then selected with B(1), collided with oxygen, and the resulting cationic species were observed by scanning E(1) with reversed polarity. Besides the charge-reversed FeS^+ (100%), we observed Fe^+ (20%) and S^+ (1%). In the process $FeS^- \rightarrow FeS^+$ two successive collision-induced electron detachments presumably take place [Eqs. (1) and (2)]. The minimum energy

$$FeS^- \longrightarrow FeS + e^- \qquad (1)$$

$$FeS \longrightarrow FeS^+ + e^- \qquad (2)$$

requirements of reactions (1) and (2) correspond to EA(FeS) and IE(FeS), respectively, and these energies are provided by the kinetic energy of the projectile (8 keV). Therefore, the charge-reversed FeS^+ signal appears at a slightly lower energy than the incident FeS^- precursor, and to a first approximation, the energy difference (ΔE) between the high-energy onsets of both peaks corresponds to the sum of the EA and IE of neutral FeS. Experimentally, the energy loss ΔE was determined as 10.0 ± 0.5 eV; the experimental error is essentially a consequence of the low signal-to-noise ratio due to the small yield of FeS^- obtained in our CI conditions. Taking EA(FeS) = 1.7 ± 0.1 eV,[21] this energy difference leads to IE(FeS) = 8.3 ± 0.6 eV.

In this type of charge-reversal experiment,[24] neutral FeS is suggested to be an intermediate which is ionized to the cation in a second step [Eq. (2)]. However, charge reversal is not a convincing proof for the accessibility of a neutral species in the gas phase. Instead, we performed a NR experiment[11] of the FeS^+ cation. Not unexpectedly, since FeS is stable in the gas phase,[23] a surviving signal of parent ion was obtained after neutralization of mass-selected FeS^+ by collision with xenon and reionization with oxygen. In the NR spectrum, the base peak was Fe^+ (100%), with about 40% of the recovery signal FeS^+ and 10% $S^{\cdot+}$.

As mentioned above, our measurement of the charge-reversal energy loss of FeS^- provides a value for the ionization energy of FeS. However, the error bars are relatively large, and we therefore also determined IE(FeS) by studying the electron-transfer properties of the FeS^+ cation in the FTICR mass spectrometer. To this end, thermalized FeS^+ cations were treated with neutral reactants with well-known ionization energies.[8b] Hence, the occurrence or absence of charge transfer provides lower and upper bounds for IE(FeS). Experimentally, electron transfer is observed from anisole (IE = 8.21 ± 0.02) to FeS^+ to yield anisole radical cation and neutral FeS, while electron transfer does not take place at all for *m*-xylene (IE = 8.56 ± 0.01) and other substrates with IEs larger than 8.6 eV. Considering the fact that under FTICR conditions the FeS^+ ions react at room temperature,[25] the thermal contributions lead to an estimate of IE(FeS) = 8.3 ± 0.2 eV.

The ionization energy of FeS^+, that is, the second ionization energy of FeS, was determined by charge-stripping (CS) mass spectroscopy[7] and leads to $IE(FeS^+) \approx Q_{min}(FeS^+) =$ 16.7 ± 0.5 eV (see below). The CS mass spectrum is dominated by the Fe^+ fragment (100%), while FeS^{2+} (3%), $S^{\cdot+}$ (2%), and Fe^{2+} (< 1%) are weak. Within the detection limit, we found no evidence for any features due to a Coulomb explosion of the dication (i.e., $FeS^{2+} \rightarrow Fe^+ + S^{\cdot+}$), such as, for example, broadening of the base of the Fe^+ and $S^{\cdot+}$ signals. These observations indicate that the FeS^{2+} dication is stable at least for the time of transit through E(1), that is, for about 6 µs. Further, no features were observed in the dication peak when it was recorded under higher energy resolution ($E/\Delta E = 4000$). Such features may arise from formation of a mixture of electronic states of the monocation in the ion source, which require different energies to undergo charge stripping.[9] Their absence in our spectra indicates that the parent FeS^+ formed under our conditions does not contain significant amounts of electronic states with excitation energies higher than about 2 eV, the limit of resolution of our experiments for FeS^+.

For comparison, we performed the same experiments for iron oxide. In the energy-resolved charge reversal, we obtained a ΔE of 10.2 ± 0.2 eV, which agrees perfectly with the sum of EA(FeO) and IE(FeO) (1.493 and 8.8 ± 0.2 eV, respectively).[26] A similar result of IE(FeO) = 8.8 ± 0.2 eV can be derived from bracketing FTICR experiments. Thus, electron transfer from *p*-chlorotoluene (IE = 8.69 ± 0.02 eV) to FeO^+ is significant, while it is very weak[27] for toluene (IE = 8.82 ± 0.01 eV) and absent for chlorobenzene (IE = 9.07 ± 0.02 eV). Further, the as yet unknown ionization energy of FeO^+ was determined by charge-stripping mass spectrometry as $IE(FeO^+) \approx Q_{min}(FeO^+) = 18.3 \pm 0.3$ eV. Like with the sulfur species, no Coulomb explosion of the dication was observed at $E/\Delta E = 8000$, nor were any features corresponding to excited states (> 1 eV) of the parent ion.

Theoretical results: A computational study of the diatomic iron chalcogenides requires a treatment at a reasonably good level of theory. Owing to the fact that the thermochemistry of anionic and neutral FeS is well-known and that $FeO^{+/0}$ has been studied theoretically before,[28,29] we restricted our ab initio study to the examination of the more difficult systems FeS^+ and FeS^{2+}.

Like the isoelectronic species FeO^+, the FeS^+ cation was found to have a $^6\Sigma^+$ ground state;[29] in a one-configuration picture, this can be represented as $1\sigma^2 2\sigma^2 1\pi^4 1\delta^2 2\pi^2 3\sigma^1$ (Fig. 1). By means of stepwise geometry optimization, the bond

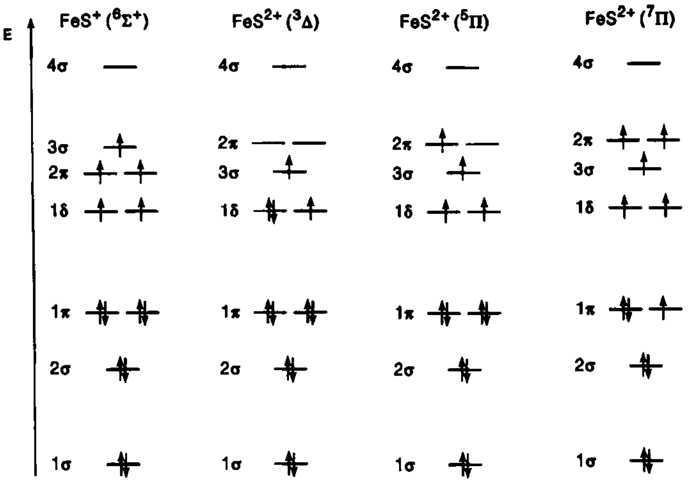

Fig. 1. Qualitative molecular orbital schemes for FeS^+ and FeS^{2+}.

length (r_{Fe-S}) was found to be 2.061 Å, with D_e = 2.81 eV, D_0 = 2.78 eV, and $\omega_e = 448\,cm^{-1}$, and a total energy of −1660.13948 Hartrees. With the enlarged basis set BS II, these values were, respectively, 2.058 Å, 2.86 eV, 2.83 eV, 447 cm^{-1}, and −1660.149221 Hartrees. Since there is no significant difference in the two groups of results obtained, we assume that the smaller basis set (BS I) is sufficient for treating the present problem. The calculated D_0 compares favorably with the experimentally determined bond energy of 2.65 ± 0.22 eV.[22]

As with the oxide species, the first excited states of FeS^+ have quartet multiplicities, namely, $^4\Pi$ and $^4\Phi$ (both $1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 2\pi^1 3\sigma^1$). These states are very close in energy and therefore quasidegenerate. The vertical excitation energy of FeS^+ ($^4\Pi$) from the sextet ground state FeS^+ ($^6\Sigma^+$) amounts to 0.42 eV, while the adiabatic splitting (r_{Fe-S} = 2.12 Å) is 0.34 eV. At the minimum geometry of the $^4\Pi$ state, the $^4\Phi$ state lies 0.03 eV higher. An additional quartet state, $^4\Delta$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^2 2\pi^2 3\sigma^1$), lies 0.41 eV above the minimum of the $^4\Pi$ state; the second $^4\Delta$ state ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 2\pi^2 3\sigma^0$) was observed to be very close in energy at the CASSCF level; this is expected to be true also at the higher level.

For the calculations of the dication surface, we first evaluated the accuracy of our computational approach (ACPF with BS I): The two dissociation asymptotes of the FeS^{2+} dication, Fe^+ (^6D) + $S^{\cdot+}$ (^4S) and Fe^{2+} (^5D) + S(^3P) were calculated as 10.12 and 15.75 eV, respectively, above the ground states of isolated Fe^+ and S. Although slightly underestimated, these figures are in reasonable agreement with the experimental data (IE(S) = 10.36 eV and IE(Fe^+) = 16.18 eV).

We then proceeded to find the lowest triplet, quintet, and heptuplet states of the FeS^{2+} dication, in the various symmetries. We found four low-lying states of FeS^{2+} of three different multiplicities: $^3\Delta$, $^5\Pi$, $^5\Delta$, and $^7\Pi$. The computed potential-energy curves (Fig. 2) reveal that energy separations between these states are small, and thus certainly, within the expected errors involved in the theoretical method. Moreover, the calculational approach used neglects relativistic effects and does not take spin–orbit coupling into account. Although the corresponding corrections are likely to be fairly small, it would clearly be unwise to draw any definitive conclusions from the present study about the ground state of the dication. Nevertheless, the spread of the energies is of similar magnitude as the experimental error bars, so that thermodynamic conclusions can be drawn within the uncertainty of experimental and theoretical results (see below).

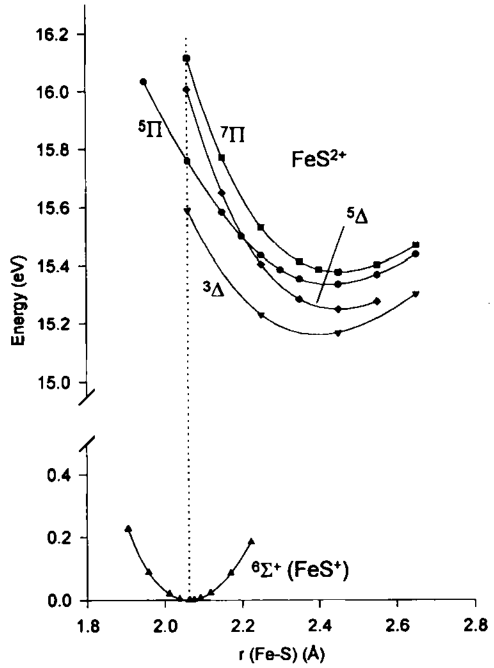

Fig. 2. Computed potential-energy curves of ground-state $^6\Sigma^+$ FeS^+ (▲), and of the $^3\Delta$ (▼) [30], $^5\Pi$ (●), $^5\Delta$ (◆), and $^7\Pi$ (■) states of FeS^{2+}.

According to the ACPF results, the lowest state is a $^3\Delta$ state ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^3 3\sigma^1 2\pi^0$) with an IE_v of 15.59 eV from ground-state FeS^+. Owing to the large number of important reference configurations in the zeroth order wavefunction, which leads to very expensive ACPF calculations, we were only able to compute a single point for this state, corresponding to the vertical ionization. The other points in Figure 2 were estimated from the corresponding CASSCF energies by adding the almost constant dynamic correlation energies.

The other low-lying states that were considered at the ACPF level of theory were $^5\Pi$ ($1\sigma^2 2\sigma^2 1\pi^4 1\delta^2 3\sigma^1 2\pi^1$), $^5\Delta$ ($1\sigma^2 2\sigma^2 1\pi^3 1\delta^3 3\sigma^1 2\pi^1$), and $^7\Pi$ ($1\sigma^2 2\sigma^2 1\pi^3 1\delta^2 3\sigma^1 2\pi^2$). For vertical ionization of FeS^+ ($^6\Sigma^+$) with r_{Fe-S} = 2.061 Å, the lowest of these, the $^5\Pi$ state, lies 15.76 eV above the monocation. To a first approximation, we consider this value as the vertical ionization energy (IE_v) of FeS^+ ($^6\Sigma^+$), because although the FeS^{2+} ($^3\Delta$) state is slightly lower in energy, formation of a triplet by ionization of a sextet ground state would require a spin flip, and is therefore improbable.

For each of the four states that we considered, the minima exhibit larger r_{Fe-S} bond lengths than the monocation. There is therefore a relaxation of the dications ranging from 0.4 to 0.7 eV from the geometry obtained by vertical ionization to the respective minima, and the lowest point in Figure 2, FeS^{2+} ($^3\Delta$) with $r_{Fe-S} \approx 2.4$ Å, is only 15.15 eV above ground-state FeS^+ ($^6\Sigma^+$). Qualitatively, this bond lengthening can be attributed to Coulombic repulsion between the considerable positive charges situated on both atoms; for example, according to Mulliken population analysis the partial charges (q) rise from q_{Fe} = 0.95 and q_S = 0.05 in the $^6\Sigma^+$ ground state of FeS^+ to $q_{Fe} \approx 1.3$ and $q_S \approx 0.6$ in FeS^{2+} ($^3\Delta$) and FeS^{2+} ($^5\Pi$).

Discussion

The results of the energy-resolved charge-reversal experiments in the sector mass spectrometer and the FTICR bracketing studies are consistent with previous data for the thermochemistry of

FeO and FeS. A minor point concerns the previously reported experimental value $D_0(\mathrm{Fe^+{-}S}) = 2.65 \pm 0.22$ eV,[22] for which our calculations suggest a slightly higher value (2.83 eV), which is also implied by $D_0(\mathrm{Fe^+{-}S}) = 2.91 \pm 0.37$ eV, derived from combining IE(FeS) and D_0(Fe–S),[23] and an older value of $D_0(\mathrm{Fe^+{-}S}) = 2.82 \pm 0.22$ eV.[31] Of particular interest is certainly the thermochemistry of the hitherto unknown iron chalcogenide dications $\mathrm{FeO^{2+}}$ and $\mathrm{FeS^{2+}}$, which can be derived in a thermochemical cycle once the adiabatic ionization energies ($\mathrm{IE_a}$) of the mono cations are known.

In charge-stripping experiments, the measured Q_{min} values roughly correspond to the vertical ionization energies ($\mathrm{IE_v}$) of the monocations. Previous studies of atomic transition-metal cations[32] have revealed that these Q_{min} values are often slightly higher (ca. 0.2 eV) than the IEs determined by optical spectroscopy. However, in the case of molecules, the measured Q_{min} value may underestimate $\mathrm{IE_v}$ due to the vibrational progressions in the mono- and the dications,[32] and we estimate this error as 0.2 eV for $\mathrm{FeO^+}$ and $\mathrm{FeS^+}$. These two corrections thus cancel, and we therefore assume that, to a first approximation, our measured Q_{min} values can be identified with $\mathrm{IE_v}$.

The theoretically predicted value for $\mathrm{IE_v(FeS^+)}$, 15.76 eV (or 15.59 eV if we consider the triplet surface), is thus slightly below the corrected experimental result of 16.7 ± 0.5 eV. In other words, the calculation underestimates the EA of the dication. This is expected since correlation is better accounted for with the more highly charged species. The main cause of inaccuracy in the calculations is likely to be the lack of correlation for the core electrons. The atomic ionization energies are presumably underestimated for the same reason (see above). A very crude correction can be effected if we consider that our computational approach underestimates the IEs of $\mathrm{Fe^+}$ and S by approximately 3%. If we assume that this quantity remains similar in the FeS molecule, we arrive at a corrected theoretical prediction of $\mathrm{IE_v(FeS^+)} \approx 16.2$ eV.

The computational study of $\mathrm{FeS^{2+}}$ shows that relaxation of the dication from the geometry obtained upon vertical ionization of $\mathrm{FeS^+}$ ($^6\Sigma^+$) to the minimum structure of $\mathrm{FeS^{2+}}$ ($^3\Delta$) is associated with an energy gain of about $\mathrm{IE_v} - \mathrm{IE_a} \approx 0.6$ eV, and we assume a similar correction for iron oxide (0.6 ± 0.1 eV). Using this correction derived from our theoretical study and the experimental figures for $\mathrm{IE_v}$, we can predict $\mathrm{IE_a(FeO^+)} = 17.7 \pm 0.4$ eV and $\mathrm{IE_a(FeS^+)} = 16.1 \pm 0.5$ eV.

According to these quantities, both $\mathrm{FeO^{2+}}$ and $\mathrm{FeS^{2+}}$ are metastable dications, in that the dissociation into $\mathrm{Fe^+} + \mathrm{X^{\cdot +}}$ (X = O, S) is exothermic: dissociation of $\mathrm{FeO^{2+}}$ into $\mathrm{Fe^+}$ and $\mathrm{O^{\cdot +}}$ releases 0.6 ± 0.4 eV and that of $\mathrm{FeS^{2+}}$ into $\mathrm{Fe^+}$ and $\mathrm{S^{\cdot +}}$ as much as 3.2 ± 0.5 eV, because IE(S) = 10.360 eV is less than IE(O) = 13.618 eV. These dissociations are, however, prevented by barriers, because the potential-energy curves have local minima (Fig. 2) due to curve-crossing of the repulsive $\mathrm{Fe^+}$ and $\mathrm{X^{\cdot +}}$ and attractive $\mathrm{Fe^{2+}} + \mathrm{X}$ curves.[7] With respect to the direct dissociation into the respective $\mathrm{Fe^{2+}} + \mathrm{X}$ asymptotes, both species are reasonably strongly bound ($D_0(\mathrm{Fe^{2+}{-}O}) = 2.0 \pm 0.5$ eV and $D_0(\mathrm{Fe^{2+}{-}S}) = 2.6 \pm 0.7$ eV). Thus, the bond dissociation energy $\mathrm{Fe^{2+}{-}S}$ is larger than that for $\mathrm{Fe^{2+}{-}O}$. This may appear unexpected at first sight, because oxygen usually binds more strongly to electropositive elements than sulfur. However, in the dications, the "soft" sulfur ligand can better share the positive charge than the electron-withdrawing, "hard" oxygen atom, so both effects become balanced in the dications $\mathrm{FeO^{2+}}$ and $\mathrm{FeS^{2+}}$.

The thermodynamic properties of the diatomic species $\mathrm{FeO^{-/0/+/2+}}$ and $\mathrm{FeS^{-/0/+/2+}}$ and the related dissociation asymptotes are summarized in Figure 3 and Table 1, which shows these data in terms of electron affinities (0th ionization energy), first and second ionization energies for FeS and FeO, and the respective bond dissociation energies D_0; the Fe atom is given for comparison.

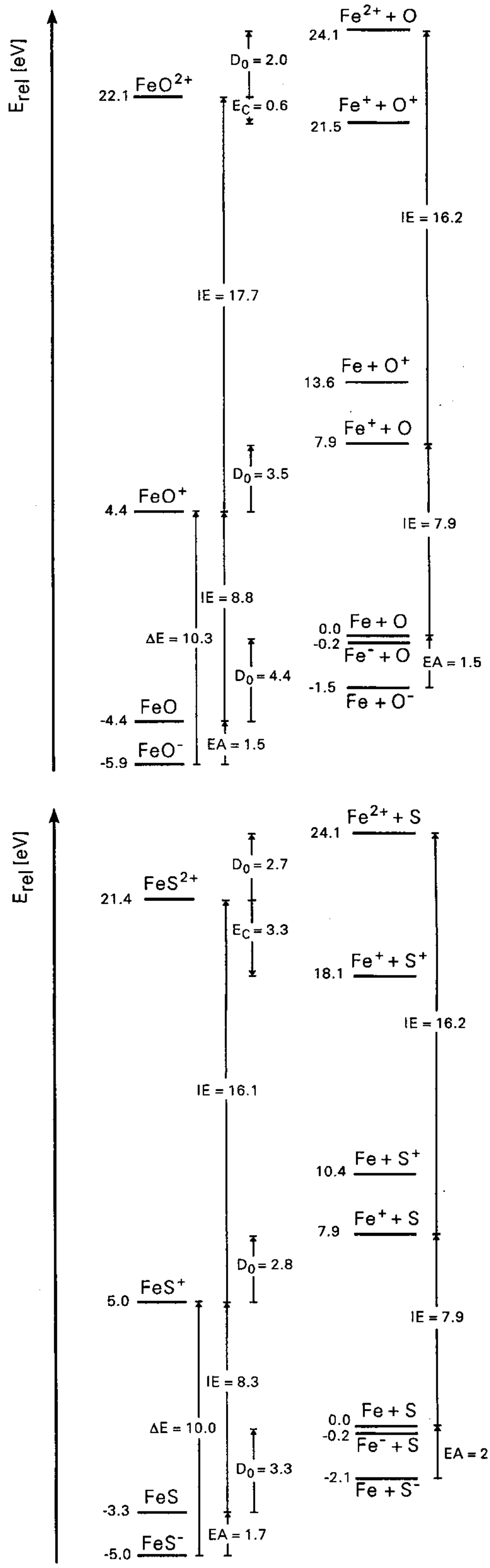

Fig. 3. Top: Thermochemistry of $\mathrm{FeO^{-/0/+/2+}}$ and the respective dissociation asymptotes (all values in eV). Bottom: Thermochemistry of $\mathrm{FeS^{-/0/+/2+}}$ and the respective dissociation asymptotes (all values in eV).

Table 1. Electron affinities (EA), ionization energies (IE), and dissociation energies (D_0) of FeX (X = O, S); data for the Fe atom are given for comparison (all values in eV).

	EA(FeX)	D_0(Fe–X)	IE(FeX)	D_0(Fe^+–X)	IE(FeX^+) [a]	D_0(Fe^{2+}–X)
Fe	0.151 [b,c]		7.9024 [b,c]		16.1820 [b,c]	
FeO	1.493 [b]	4.40 ± 0.14 [d]	8.8 ± 0.2 [d,e]	3.47 ± 0.06 [d]	17.7 ± 0.4 [f]	2.0 ± 0.5 [f]
FeS	1.7 ± 0.10 [g]	3.31 ± 0.17 [h]	8.3 ± 0.2 [f]	2.65 ± 0.22 [i,j]	16.1 ± 0.5 [f]	2.7 ± 0.7 [f]

[a] For the conversion of Q_{min} values to IE(FeX^+), see text. [b] Taken from ref. [8]. [c] For high-precision values obtained by spectroscopy their small experimental errors are neglected. [d] Taken from ref. [26]. [e] Ref. [8] gives 8.9 ± 0.1 eV; our bracketed value is 8.8 ± 0.2 eV. [f] This work. [g] Taken from ref. [21]. [h] Taken from ref. [23]. [i] Taken from ref. [22]. [j] Computationally, we predict 2.83 eV, see text.

With respect to the role of iron oxides and iron sulfides in the condensed phase, the results reported here allow a discussion of the intrinsic effects of a ligating oxygen or sulfur atom on the redox chemistry of bare iron in a broad range of oxidation states. As can be seen from the data in Table 1, ligation of iron atom with the chalcogenides oxygen or sulfur leads to more electron-attracting species than the bare atom, in all the oxidation states considered (i.e., higher EAs and IEs than for the bare metal). The more important trend, however, is that relating the oxygen and sulfur species: it can be seen that the FeS^- anion and the two FeS cations are all more stable than the corresponding oxide ions, that is, EA(FeS) > EA(FeO), IE(FeS) < IE(FeO), and IE(FeS^+) < IE(FeO^+). As a general conclusion neutral FeS is more readily reduced and oxidized in the gas phase than FeO; iron sulfide thus can attain its various oxidation states with greater ease than the oxide.

Conclusions

We have been able to derive a complete set of thermodynamic data of FeS and FeO in the gas phase by using various mass-spectrometric techniques and complementary high-level ab initio methods. These data allow a direct comparison of the intrinsic redox properties of diatomic iron oxide and sulfide, which shows that redox processes are more favorable for FeS than for FeO over a the whole range of oxidation states that are accessible in the gas phase. Thus, also at the molecular level, iron sulfides seem to better adapted for electron transfer processes than the oxides.[33]

Furthermore, we have established the existence and stability of two new diatomic dications. From the measured ionization energies of the monocations, it is shown that both FeS^{2+} and FeO^{2+} are metastable species; however, exothermic Coulomb explosions into Fe^+ and $X^{\cdot +}$ (X = O, S) are prevented by kinetic barriers, and thus do not take place spontaneously.

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