



Fe2: As simple as a Herculean labour. Neutral (Fe2), cationic (Fe2 +), and anionic (Fe2 -) species

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Fe₂: As simple as a *Herculean* labour. Neutral (Fe₂), cationic (Fe₂⁺), and anionic (Fe₂⁻) species

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We have studied 175 molecular states of the Fe₂ diatomic by constructing full potential energy curves dissociating to the ground Fe(⁵D) + Fe(⁵D) and first excited Fe(⁵D) + Fe(⁵F) dissociation channels by multireference configuration interaction methods and large basis sets. The ground $X^9\Sigma_g^-$ and the first excited ${}^7\Sigma_u^-$ states have been detailed by a multitude of plain and explicitly correlated F12 methods at both the valence and core-valence computational levels. The potential curves of most of the states present strong interactions/avoided crossings that trigger a severe non adiabatic behavior. For reasons of completeness, the ground states of the charged Fe₂^{-,+} species have also been considered. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922793]

I. INTRODUCTION

Stone Age is a broad prehistoric period during which stone was widely used. This period lasted roughly 3.4 million years and ended around 3000 BCE with the advent of metal working. After a short period of roughly 2000 years during which copper and bronze were used, a third age began—the Iron Age.

Pure iron is softer than bronze and therefore produces tools which wear out faster. The advantage of using iron over bronze lies in cheaper production and the wide availability of iron ore. But iron smelting was more difficult than tin and copper, so it is not surprising that humans only mastered iron metallurgy after some millennia of bronze metal working.

Not only in everyday life and war but also biologically iron plays crucial roles in the transport and storage of oxygen and also in electron transport, and it is safe to say that, with only a few exceptions in the bacterial world, there would be no life without it.

Although iron has played a crucial role in mankind during the last 4000 years, what do we really know about the simplest and the most elementary entity, the iron dimer? Curiously enough what we really know is very little, inversely proportional to its huge impact in human civilization.

The existing literature is limited to a handful of papers dating back in 1969 when Lin and Kant¹ used a combination of Knudsen effusion and mass spectrometric techniques to identify Fe₂ and establish its dissociation energy. The latter was found to be equal to $D_0^o = 19.7$ and 30 ± 5 kcal/mol based on the second- and third-law methods, respectively.

Some years later, de Vore *et al.*² observed electronic absorption bands in the visible spectral region for Fe_2 in Ar matrices at 10 K. They assigned the three observed transitions

to A \leftarrow X ($\Delta G'_{1/2} = 194 \text{ cm}^{-1}$), B \leftarrow X ($\Delta G'_{1/2} = 218 \text{ cm}^{-1}$), while the third C \leftarrow X one is a continuous absorption with maximum at 4145 Å.

In 1975, Montano et al.³ reported Mössbauer spectrum data showing magnetic hyperfine interactions for both isolated iron monomers and dimers in solid Ar with an applied external magnetic field. The large internal magnetic field demonstrated by this study established that Fe₂ has a large spin or orbital angular momentum. Another result of their work that should be seriously considered is that V_{gg} is negative. Based on a simple crystal field approach for the ground ⁵D Fe state, they concluded that only the $|3z^2 - r^2\rangle$ level (Σ symmetry in the molecular case) gives the right magnitude and sign of the quadrupole splitting indicating that this is the ground state. Since this level contributes nothing to the hyperfine magnetic field, it is the spin angular momentum responsible for the internal field. The above analysis seems to explain qualitatively the experimental results although, as the authors stress, one should be careful in using crystal field theory to analyze the Fe₂ molecule.

The molecular constants of ⁵⁶Fe₂, $\omega_e = 299.6 \text{ cm}^{-1}$, and $\omega_e x_e = 1.4 \text{ cm}^{-1}$ were recorded for the first time through resonance Raman spectroscopy in solid Ar and Kr matrices⁴ while an internuclear distance $r_e = 2.02 \pm 0.02$ Å was deduced from rare gas matrix isolation techniques in combination with extended X-ray absorption fine structure (EXAFS) studies in solid Ne matrices.⁵ Earlier EXAFS measurements in solid Ar matrices gave a value of $r_e = 1.87 \pm 0.13$ Å.⁶

The very first *ab initio* study beyond the Hartree–Fock (HF) level was by Shim and Gingerich⁷ who carried out all electron configuration interaction (CI) calculations for 112 electronic states based on the HF orbitals of a $^{7}\Sigma_{u}^{+}$ state coupled with a (14s11p5d/8s6p3d) basis set. All states studied resulted from the interaction of two excited Fe(⁵F) atoms at r = 4.691 bohrs. The proposed ground state is of $^{7}\Delta_{u}$ symmetry with a configuration

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$$(4s\sigma_g)^{2.00}(3d\sigma_g)^{1.57}(3d\sigma_u)^{1.49}(3d\pi_u)^{3.06}(3d\pi_g)^{2.89}(3d\delta_u)^{2.47}(3d\delta_g)^{2.53},$$

featuring a single bond, $r_e = 4.54$ bohr, a binding energy $D_e = 0.69$ eV relative to two excited Fe(⁵F) atoms, and $\omega_e = 204$ cm⁻¹. We should mention though that they failed to converge to states dissociating to Fe(⁵D) + Fe(⁵F), the first excited adiabatic channel, to which most of their calculated states should have correlated. The results of this *ab initio* study of Fe₂ were used to obtain an improved estimate of the entropy of Fe₂ at the high temperatures of the Knudsen effusion mass spectrometric studies, permitting a revision of the third law value of the Fe₂ bond energy. The revised value, $D_0^o = 18 \pm 4$ kcal/mol, is in much better agreement with the second law value obtained by Lin and Kant, 19.7 ± 5 kcal/mol.¹

Rare gas matrix isolation techniques have been used in conjunction with Mössbauer spectroscopy to study Fe₂ by Nagarathna *et al.*⁸ They have measured parameters such as quadrupole splitting and isomer shift. SCF–Xa–scattered wave functions were employed to calculate the necessary one electron properties in order to calculate the experimental Mössbauer values. Two candidates for the ground state are the ${}^{7}\Sigma_{g}$ and ${}^{9}\Sigma_{g}$ symmetries (± symmetry was not defined in the study), with the ${}^{9}\Sigma_{g}$ state being lower in energy. They finally proposed the ${}^{7}\Sigma_{g}$ as the most probable ground state based on the bond order and the experimental value of the stretching force constant.

In 1984, Baumann, Van Zee, and Weltner⁹ published an ESR study on MnAg, CrZn, and diatomics attempted but not observed since these were believed to be prepared, and they discussed their likely lowest electronic states. This study along with Ref. 3 is of crucial importance in the subsequent studies since they triggered a way of thinking based unfortunately on a number of assumptions, conjectures, and speculations. Fe2 is clearly not observed in the ESR spectrum but the authors have chosen to speculate about its ground state. Three possibilities were suggested to account for the absence of an ESR spectrum: (1) the molecule was not formed in the matrices, (2) it has S = 0 or an orbitally degenerate ground state (*i.e.*, $\Lambda \neq 0$), and (3) it has a zero-field splitting parameter, D, that is so large that transitions between the different Ω -levels of the $^{2S+1}\Sigma$ ground state are unobservable using X-band microwave radiation for excitation. The first hypothesis was dismissed as being unlikely. If D is not large then all Σ ground states should be detectable, provided that $S \neq 0$. If $S \neq 0$ and $\Lambda \neq 0$, then the state will be unobservable regardless of the D value. For odd spin multiplicities of Σ states, a large D value could prevent an ESR signal. Based on the above and the conclusions of Ref. 3, they proposed two symmetries as the most probable, the $^{7}\Delta$ or $^{7}\Sigma$, but finally they suggested that the X state is of $^{7}\Delta$ symmetry assuming that D is positive and less than about 8 cm^{-1} .

A third experimental work that played a decisive role in all subsequent studies is the first and only gas phase electronic spectra of Fe₂ obtained by photoelectron spectroscopy of the corresponding negative ion by Leopold and Lineberger.¹⁰ Their results can be synopsized in the following numerical data: $EA(Fe) = 0.151 \pm 0.003 \text{ eV}$, $EA(Fe_2) = 0.902$

 $\pm 0.008 \text{ eV}, \quad \omega_e(\text{Fe}_2^-) = 250 \pm 20 \text{ cm}^{-1}, \quad \omega_e(\text{Fe}_2) = 300 \pm 15 \text{ cm}^{-1}, \text{ and } \Delta r_e = r_e(\text{Fe}_2^-) - r_e(\text{Fe}_2) = 0.08 \pm 0.02 \text{ Å},$ while an excited Fe₂ state is observed at 0.534 ± 0.004 eV.

Soon after, Leopold *et al.*¹¹ published a paper with the aim to fit the experimental findings into a chemical bonding story for the X state of Fe₂. They have concluded that the photoelectron spectrum of Fe₂⁻ can be interpreted in terms of an electron detachment from the $4s\sigma_u$ orbital of a $(4s\sigma_g)^2(4s\sigma_u)^2(3d)^{13}$ anionic state. This implies a $(4s\sigma_g)^2(4s\sigma_u)^1(3d)^{13}$ neutral state correlating to one ground $(4s^23d^6)$ and one excited $(4s^{1}3d^7)$ Fe atoms.

In a couple of papers, Tomonari and Tatewaki¹² and Noro et al.¹³ investigated the ground state of Fe_2 through CI and multireference configuration interaction (MRCI) calculations, respectively. In both papers, a very small number of $^{7}\Lambda$ symmetries were considered, and the $^{7}\Delta_{\mu}$ one popped up as the lowest one. This state correlates to two Fe(⁵F) atoms and has a $\sim 3d^{14}$ molecular configuration since the investigators failed to converge to states dissociating to the first excited adiabatic channel of mixed ⁵D/⁵F character. It is worthy to notice that their calculated D_e with respect to two ⁵F Fe atoms is 0.94 eV, while it is -1.29 eV relative to two ⁵D atoms¹² but based on tailor-made large scale CI calculations, they obtained a $D_e = 0.38(1.57)$ eV with respect to two ⁵D Fe atoms at the CI(+Q) level of theory.¹³ The proposed $\sim 3d^{14}$ molecular configuration is in disagreement with the simple interpretation advocated by Leopold *et al.*¹¹

There are two *ab initio* studies that appeared practically simultaneously and are perhaps the first serious theoretical attempts to decipher the Fe2 case, the first one by Bauschlicher and Ricca (BR)¹⁴ and the second one by Hübner and Sauer (HS).^{15,16} BR¹⁴ used mainly MRCI and second order perturbation theory (CASPT2) methods and found that the ${}^{9}\Sigma_{o}^{-}(\sim d^{13})$ state was the lowest one, while the ${}^{7}\Delta_{u}(\sim d^{14})$ state was found to lie just 2445 cm⁻¹ higher. Although their calculations yield a ${}^{9}\Sigma_{g}^{-}$ ground state consistent with many of the observations from the photo detachment spectra, it is inconsistent with the way they have interpreted the ESR findings and their r_e value is different than the EXAFS one. So, they proposed a ${}^{7}\Delta_{u}$ ground state although this is not compatible with the photoelectron spectra. They suggested a scenario that could explain all of the experimental observations and that admits a $X^{8}\Sigma_{\mu}^{-}(\text{Fe}_{2}^{-})$ state with the two states observed in the photodetachment spectra being of ${}^{9}\Sigma_{g}^{-}$ and ${}^{7}\Sigma_{g}^{-}$ symmetry but the X Fe₂ state is nevertheless a ${}^{7}\Delta_{\mu}$ one but not observed due to symmetry reasons.

HS¹⁵ on the other hand emphatically concluded that the ground states of Fe₂ and Fe₂⁻ are of ${}^{9}\Sigma_{g}^{-}$ and ${}^{8}\Sigma_{u}^{-}$ symmetry, respectively, with molecular parameters consistent with the available experimental data. They presented partial potential energy curves (PECs), but they did not provide any dissociation energies and did not consider at all the ESR results.

In 2009, Casula *et al.*¹⁷ presented Monte Carlo (MC) simulations based on a resonating valence bond (RVB)

wave function. They performed variational and diffusion MC calculations and obtained a ${}^{9}\Sigma_{g}^{-}$ Fe₂ and a ${}^{8}\Sigma_{u}^{-}$ Fe₂⁻ as ground states. Although their findings were in agreement with the photoelectron spectra, when they corrected the energetics to account for the experimental atomic splitting, the ${}^{7}\Delta_{u}$ state was found to be the ground state.

In 2011, Angeli and Cimiraglia¹⁸ published a multireference perturbation theory study of only two Fe₂ states, the ${}^{9}\Sigma_{g}^{-}$ and the ${}^{7}\Delta_{u}$, since these two are the most probable candidates for the ground state. They produced PECs displaying discontinuities but nevertheless the ${}^{9}\Sigma_{g}^{-}$ was always lower in energy. The root of the problems encountered was attributed to the inadequate active space suggesting that the doubling of the *d* orbitals in each atom would eventually resolve them. They finally concluded their work as partially satisfactory.

The last work on Fe₂ is the very recent publication by Hoyer *et al.*,¹⁹ who employed the restricted active space self consistent field (RASSCF) method followed by second order perturbation theory and rather large active spaces including the plain valence 4*s* and 3*d*, and five more 3*d'* and three 3*p'* additional orbitals on each atom. They have constructed the ${}^{9}\Sigma_{g}^{-}$ state's PEC that erroneously dissociates to two ground state atoms. According to the Wigner and Witmer rules, there is no state of ${}^{9}\Sigma_{g}^{-}$ symmetry correlating to Fe(⁵D) + Fe(⁵D); see Figs. 1 and 2 of Ref. 19. The avoided crossing and the associated barrier discussed in their Sec. III B are both an artifact. Actually, there is not any avoided crossing within the Λ -S scheme. At large inter nuclear distances, their PEC is part of a ${}^{9}\Delta_{g}$ state having the same D_{2h} symmetry as the ${}^{9}\Sigma_{g}^{-}$ state. Moreover, the molecular parameters extracted are not in good agreement with the experimental data (see Table IV of Ref. 19).

We should notice at this point that in all previous computational works, only a very limited number of states have been studied while no reference to those dissociating to two ground state Fe atoms has been made and consequently their interaction with the ones studied is unknown. The present study will reveal their key role in the appearance and dramatic non adiabatic behavior of the bound states due to the "innocent" and perhaps uninteresting van der Waals (vdW) $4s^2 3d^6 \leftrightarrow 4s^2 3d^6$ states.

It is more evident by now that not only the limited experimental work but also theoretical work on that species is closely interconnected and trapped into each other's assumptions.

As part of our in going interest in transition metal diatomics, *i.e.*, Sc₂,²⁰ Ti₂,²¹ TiFe,²² ScTi,²³ and Mn₂,²⁴ we presently offer the first exhaustive panoramic view of the smallest iron cluster, Fe₂, by constructing full PECs for all 175^{2S+1}A states dissociating to the ground Fe(4*s*²3*d*⁶; ⁵D) + Fe(4*s*²3*d*⁶; ⁵D) and first excited Fe(4*s*²3*d*⁶; ⁵D)+Fe(4*s*¹3*d*⁷; ⁵F) dissociating channels by MRCI techniques. The molecular states studied are the following:

$$Fe(4s^{2}3d^{6}; {}^{5}D) + Fe(4s^{2}3d^{6}; {}^{5}D) \xrightarrow{75 \text{ states}} {}^{1,5,9}(\Sigma_{g}^{+}[3], \Sigma_{u}^{-}[2], \Pi_{g}[2], \Pi_{u}[2], \Delta_{g}[2], \Delta_{u}, \Phi_{g}, \Phi_{u}, \Gamma_{g}) \text{ and} \\ \xrightarrow{3,7}(\Sigma_{u}^{+}[3], \Sigma_{g}^{-}[2], \Pi_{g}[2], \Pi_{u}[2], \Delta_{g}, \Delta_{u}[2], \Phi_{g}, \Phi_{u}, \Gamma_{u}) \\ Fe(4s^{2}3d^{6}; {}^{5}D) + Fe(4s^{1}3d^{7}; {}^{5}F) \xrightarrow{100 \text{ states}} {}^{1,3,5,7,9}(\Sigma^{+}[2], \Sigma^{-}[3], \Pi[5], \Delta[4], \Phi[3], \Gamma[2], H)_{u} \text{ and } g.$$

As expected, and also supported by our recent experience, all 75 states originating from two ground state Fe atoms are of vdW type and thus chemically uninteresting, but what turns out to be extremely intriguing is their interaction with the chemically bound ${}^{2S+1}\Lambda$ states correlating to the first excited adiabatic channel. Most of these 100 states have strong to extremely strong interactions/avoided crossings with the repulsive part of the 75 vdW states, while the PECs of many of the most bound states appear completely shredded, causing most if not all of their vibrational levels to predissociate.

For reasons of completeness and comparison with the available experimental data, we have also studied the ground states of both $\operatorname{Fe}_2^-(X \, {}^8\Sigma_u^-)$ and $\operatorname{Fe}_2^+(X \, {}^8\Sigma_u^-)$ species.

The present work not only offers a complete roadmap to this poorly known molecule but we hope that it will also lead to new theoretical and experimental research initiatives.

II. COMPUTATIONAL DETAILS

We have employed a variety of methods and basis sets in order to properly account for the Fe_2 species. In

particular, we have used the plain MRCI in its internally contracted version²⁵ and the explicitly correlated MRCI–F12 method,²⁶ a size extensive modification of the MRCI method, namely, the MR averaged quadratic coupled cluster (AQCC) method,²⁷ the restricted coupled cluster + single + double + perturbative connected triplets (RCCSD(T)),²⁸ and its explicitly correlated version RCCSD(T)–F12²⁹ at both the valence (16e⁻) and core-valence (32e⁻) correlation levels. Scalar relativistic effects were considered through the second order Douglas–Kroll–Hess (DKH2) approximation.³⁰

A variety of correlation consistent basis sets³¹ have been used, namely, the cc–pVQZ,³² aug–cc–pVQZ,³² cc– pwCVQZ–NR³² and –DK³² and the aug–cc–pwCV(T,Q)Z– NR³² and –DK.³² For the explicitly correlated calculations, the F12 integrals can only be computed using density fitting (DF) approximations while the many electron integrals are estimated by resolutions of the identity (RI) approximations. Thus, we were forced to use three different basis sets: the atomic orbital (AO) basis, the DF (DF basis and DF basis for Fock and exchange matrices), and the RI basis, suitably chosen for the particular type of calculations envisaged (*vide infra*). The one electron basis set was issued from state averaged (SA) complete active space self consistent field (CASSCF) wavefunctions obtained by distributing all valence 16 electrons in all valence $6 \times 2 = 12$ orbitals correlating at infinity to the usual 4s + 3d atomic orbitals.

All calculations were performed under D_{2h} symmetry restrictions with the MOLPRO 2012.1 program.³³

III. RESULTS AND DISCUSSION

A. Fe₂

We have constructed full PECs for all 175 $^{2S+1}\Lambda$ states correlating to Fe($4s^23d^6$; ⁵D) + Fe($4s^23d^6$; ⁵D) and to Fe($4s^23d^6$; ⁵D) + Fe($4s^13d^7$; ⁵F). Since this number is truly immense, we have decided to present in some detail the ground and four of the lowest lying ones, while all PECs are displayed in the supplementary material³⁴ section of this paper without any further discussion.

Table IS³⁴ collects the absolute energies of the ground $Fe(4s^23d^6; {}^5D)$ and the first excited $Fe(4s^13d^7; {}^5F)$ states in a multitude of methods and basis sets along with their energy gap. To the best of our knowledge, explicitly correlated F12 results are novel for both Fe and Fe₂, and we think that Table IS³⁴ will prove valuable in assessing the quality of both methods and basis sets. Table I gathers numerical results on five Fe₂ states at the state averaged MRCI(+Q)/cc–pVQZ level of theory, while Table II details the ground and first excited states in a variety of methods. Finally, Table III presents results on the charged Fe⁻₂ and Fe⁺₂ species.

Figures 1–5 display all ${}^9\Lambda$, ${}^7\Lambda$, ${}^5\Lambda$, ${}^3\Lambda$, and ${}^1\Lambda$ states, respectively, while in Figure 6, the ground $X \, {}^9\Sigma_g^-$ along with the four lowest states $(2 \, {}^7\Sigma_u^-, 3 \, {}^7\Sigma_g^-, \text{and } {}^7\Delta_g / {}^7\Delta_u)$ are detailed when their asymptotic channels are properly displaced so that their energy gap matches the experimental $\Delta E({}^5F \leftarrow {}^5D)$

value. A ${}^{9}\Pi_{g}$ vdW state is also shown since its Ω components predissociate the higher vibrational levels of the X state. Finally, all 175 PECs are shown in 30 figures in the supplementary material³⁴ according to their spin-space (D_{2h}) symmetry. Before further proceeding to the discussion, we should comment on the energetics of the asymptotic channels displayed in Figs. 1–5. It is rather evident that the ${}^{9}\Lambda$ states dissociating to two Fe(⁵D) states are better described within the chosen active space than the rest of the spin multiplicities due to their highest number of the singly occupied orbitals. The MRCI supermolecule energy of these nonet states equals $-2525.262 E_h$ very close to the sum of the MRCI atomic fragments $(-2525.269 E_h)$, while for the rest of the spin multiplicities, the supermolecule energy is around $-2525.255 \pm 0.002 E_h$ (see Figs. 2–5) due to the increased number of the doubly occupied orbitals reaching a maximum for the ${}^{1}\Lambda$ ones. It is also quite unfortunate that all ${}^{9}\Lambda$ states dissociating to the first excited, ${}^{5}D + {}^{5}F$, channel are asymptotically described worse than the $^{7,5,3,1}\Lambda$ ones by roughly 5 mE_h, *i.e.*, the MRCI energies are $-2525.207 E_h$ $({}^{9}\Lambda)$ vs. $-2525.212 E_h ({}^{7,5,3,1}\Lambda)$. It is for these reasons that an orbital doubling³⁸ may be in order but is computationally intractable and demands extreme care with respect to the choice of the proper active space for every single molecular state envisaged.³⁹

All 75^{2S+1}A states dissociating to two Fe(⁵D) states are of vdW type, as expected due to the $4s^2 \leftrightarrow 4s^2$ repulsion, with a well depth of *circa* 130 cm⁻¹.

The ground state of Fe₂ is without any doubt of ${}^{9}\Sigma_{p}^{-}$ symmetry in agreement with previous *ab initio* results^{14,15,18,19} and with the limited experimental data when carefully considered.^{3,8} It correlates adiabatically to the mixed asymptote $|4s^{2}3d^{6}; {}^{5}D, M_{L} = \pm 2\rangle \otimes |4s^{1}3d^{7}; {}^{5}F, M_{L} = \pm 2\rangle$ while its PEC suffers an avoided crossing with a second ${}^{9}\Sigma_{p}^{-}$ state at around r = 10 bohr so its main equilibrium configurations are

$$\begin{split} \left| X^{9} \Sigma_{g}^{-} \right\rangle &\cong 0.86 \left| \begin{array}{l} 1\sigma_{g}^{+}(4s)^{2} \sigma_{g}^{+}(3d_{z2})^{2} 1\delta_{g}(3d_{x^{2}-y^{2}}) 1\pi_{u}^{2}(3d_{xz}) 1\pi_{u}^{2}(3d_{yz}) 1\delta_{g}(3d_{xy}) \\ 1\sigma_{u}^{+}(4s) 2\sigma_{u}^{+}(3d_{z2}) 1\delta_{u}(3d_{x^{2}-y^{2}}) 1\pi_{g}(3d_{xz}) 1\pi_{g}(3d_{yz}) 1\delta_{u}(3d_{xy}) \\ &+ 0.27[\left| 1\sigma_{g}^{+2} 2\sigma_{g}^{+} 1\delta_{g,x^{2}-y^{2}} 1\pi_{u,x} 1\pi_{u,y}^{2} 1\delta_{g,xy} 1\sigma_{u}^{+2} 2\sigma_{u}^{+} 1\delta_{u,x^{2}-y^{2}} 1\pi_{g,x}^{2} 1\pi_{g,y} 1\delta_{u,xy} \right\rangle \\ &- \left| 1\sigma_{g}^{+2} 2\sigma_{g}^{+} 1\delta_{g,x^{2}-y^{2}} 1\pi_{u,x}^{2} 1\pi_{u,y} 1\delta_{g,xy} 1\sigma_{u}^{+2} 2\sigma_{u}^{+} 1\delta_{u,x^{2}-y^{2}} 1\pi_{g,x} 1\pi_{g,y}^{2} 1\delta_{u,xy} \right\rangle] \end{split}$$

with corresponding Mulliken atomic distributions (the "/" separates atomic distributions in bonding/antiboding molecular orbitals)

$$\begin{split} &4s^{1.89}4p_z^{0.09}3d_{z^2}^{1.77}4p_x^{0.04}3d_{xz}^{1.81}4p_y^{0.04}3d_{yz}^{1.81}3d_{x^{2-y^2}}^{1.0}3d_{xy}^{1.0}/\\ &4s^{0.69}4p_z^{0.34}3d_{z^2}^{1.16}4p_x^{0.01}3d_{xz}^{1.13}4p_y^{0.01}3d_{yz}^{1.13}3d_{x^{2-y^2}}^{1.0}3d_{xy}^{1.0}. \end{split}$$

The "0.86" component reflects the (0,0) combination of the ⁵D + ⁵F mixed asymptote that gives rise to a ${}^{9}\Sigma_{g}^{-}$ symmetry in contrast to $|{}^{5}D,M_{L} = 0\rangle \otimes |{}^{5}D,M_{L} = 0\rangle$ that generates a ${}^{9}\Sigma_{e}^{+}$ one. The bonding situation can be visually represented by a valence bond Lewis diagram.



The $3d_{\delta}$ electrons are strictly localized but there is a small delocalization of the $3d_{\pi}$ and $3d_{\sigma}$ electrons despite

TABLE I. Energies $E(E_h)$, bond distances $r_e(Å)$, harmonic frequencies $\omega_e(cm^{-1})$, anharmonic corrections $\omega_e x_e(cm^{-1})$, adiabatic dissociation energies $D_e(kcal/mol)$ and energy gaps $T_e(kcal/mol)$ of the $X \, {}^9\Sigma_g^-$, $2^7 \Sigma_u^-$, $3^7\Sigma_g^-$, $4^7 \Delta_u$, and $5^7 \Delta_g$ states of ${}^{56}Fe_2$ at the state averaged MRCI(+Q)/cc–pVQZ level of theory, experimental results in square brackets.

State	-Е	r _e	ω_e	$\omega_e \mathbf{x}_e$	D_e	T_e
$X^{9}\Sigma_{g}^{-}$	2525.243 585	2.192.01	244.41	0.482	22.51	0.0
	(2525.321231)	(2.081 14)			(31.5)	(0.0)
		$[1.87 \pm 0.13]^{a}$	[299.6] ^b	[1.4] ^b	$[30 \pm 5]^{c}$	
		$[2.02 \pm 0.02]^{d}$	$[300 \pm 15]^{e}$		$[19 \pm 7]^{t}$	
			[299.5] ^g	[1.31] ^g	$[23 \pm 5]^{h}$	
					$[25 \pm 5]^{i}$	
					$[18 \pm 4]^{j}$	
					$[35.1 \pm 0.6]^{k}$	
					$[26.52 \pm 2.08]^{1}$	
					[26.52] ^m	
					[26.82] $[26.29 \pm 2.31]^{\text{n}}$	
					$[20.29 \pm 2.51]$	
$2^{7}\Sigma_{u}^{-}$	2525.234 602	2.282 31	227.34	2.798	14.17	5.64
	(2525.302442)	(2.192 81)	(373.30)	(8.868)	(22.16)	(11.79)
$3^7 \Sigma_g^-$	2525.232 039	2.176 55	287.38	3.891		7.25
0	(2525.299 233)	(2.15036)	(395.30)	(3.475)		(13.80)
						$[12.31 \pm 0.09]^{e}$
$4^{7}\Delta_{u}$	2525.231 030	2.339 02	92.21	1.573		7.88
	(2525.297 541)	(2.219 10)	(180.26)	(4.825)		(14.87)
$5^{7}\Delta_{\sigma}$	2525.229 054	2.418 14	181.10	3.600		9.12
0	(2525.292962)	(2.301 15)	(316.49)			(17.74)

^aEXAFS measurement.⁶

^bResonance Raman spectroscopy.⁴ A $D_c(=\omega_c^2/4\omega_c x_c) = 45.8$ kcal/mol can be calculated, compare with the diabatic dissociation energy (DDE = 46.35 kcal/mol) given in Ref. 42

^cDissociation energy (D₀^o) based on the third law.¹

dEXAFS measurement.5

^eNegative ion photoelectron spectroscopy.¹⁰

^fDissociation energy (D₀^o) based on the second law.¹

^gFitting the data of Ref. 4 to a Dunham expansion.⁴¹

^hDissociation energy (D_0^{o}) based on the third law and on ¹⁵A states.¹

ⁱ Dissociation energy (D_0^0) based on the third law and on ${}^9\Lambda$ states.¹

^j Dissociation energy (D0°) based on the third law.⁷

^kDissociation energy (D₀^o) based on the assumptions of Ref. 1. ⁷

¹Dissociation energy (D⁰) based on collision induced dissociation studies of gas phase Fe₂⁺. A diabatic dissociation energy (DDE)

is also given, $DDE = 46.35 \text{ kcal/mol.}^{42}$

^mReference 41.

ⁿDissociation energy (D^o) based on collision induced dissociation studies of gas phase Fe2^{+,43}

their smaller size with respect to the 4s orbital, $\langle r \rangle_{4s} / \langle r \rangle_{3d} = 3.04^{40}$

The same type of bonding has been observed in the $Sc_2(X {}^5\Sigma_u)^{20}$ and $Ti_2(2 {}^7\Sigma_u^+$ and $3 {}^3\Sigma_u^+)^{21}$ molecular systems with one of the atoms being in an excited $4s^{1}3d^{n+1}$ configuration. The minimum (see Fig. 1) of its PEC lies just 4138 cm^{-1} above the ${}^{5}D + {}^{5}D$ channel while it crosses the PEC of a ${}^{9}\Pi_{g}$ state at $\sim 1400 \text{ cm}^{-1}$ above its minimum. This is rather of crucial importance since its ro-vibrational levels at around this and higher energies will be predissociated through spin-orbit interaction. When the PEC of the ground state is downshifted by ~2860 cm⁻¹ with respect to the $^{7}\Lambda$ manifold in order to match the experimental $\Delta E({}^{5}F \leftarrow {}^{5}D) = 7056.79 \text{ cm}^{-1}$ energy gap,³⁷ then its minimum lies lower than the ${}^{5}D + {}^{5}D$ asymptote by 828 cm⁻¹, see Fig. 6. Had we calculated the mixed asymptote in its experimental value, the $X \, {}^9\Sigma_g^-$ state would certainly lie below the ground dissociation channel by at least $2860 + 828 = 3688 \text{ cm}^{-1}$. And this is indeed the case even at the MRCI+Q/cc-pwCVQZ level of theory; the state is bound

by only 3.8 kcal/mol (see Tables IS³⁴ and II). This tendency gets more pronounced at the RCCSD(T)/cc-pwCVQZ level of theory; the $X {}^9\Sigma_g^-$ state gets lower than two Fe(⁵D) atoms by 12.5 kcal/mol or 14.4 kcal/mol when corrected for the experimental $\Delta E({}^5F \leftarrow {}^5D)$ energy gap, see Tables IS³⁴ and II. Based on the occupation numbers of the MRCI natural orbitals, we augmented the active space of the reference wavefunction by three orbitals of σ_g^+ and $\pi_u(x \text{ and } y)$ symmetry. The "augmented" MRCI(+Q)/cc-pwCVQZ results are E= -2525.280 396(-2525.354 271) E_h, \mathbf{r}_e = 2.177 80 (2.184 34) Å, ω_e = 307.87 (318.73) cm⁻¹, and D_e^0 = 14.50 (29.20) kcal/mol while the adiabatic binding energy is D_e = 36.02 (49.67) kcal/mol. The latest experimental value for the dissociation energy is D^o = 26.29 ± 2.31 kcal/mol.⁴³

Our equilibrium distance ranges from 2.08 Å (Table I) to 2.18 Å (Table II) with the C–RCCSD(T)–DK value being 2.101 Å (Table II) $[r_e(exp) = 2.02 \pm 0.02 \text{ Å}^5]$. In most of the cases, our ω_e value compares nicely with the experimental one of 299.6 cm^{-1.4} At this point, we should also comment on

TABLE II. Energies $E(E_h)$, bond distances $r_e(Å)$, harmonic frequencies $\omega_e(cm^{-1})$, anharmonic corrections $\omega_e x_e(cm^{-1})$, adiabatic dissociation energies $D_e(kcal/mol)$ and energy gaps $T_e(kcal/mol)$ of the $X \, {}^9\Sigma_g^-$ and the $2 \, {}^7\Sigma_u^-$ states of ${}^{56}Fe_2$ at different levels of theory.

State	Method	-Е	r _e	ω_e	$\omega_e \mathbf{x}_e$	D_e^a	T_e
X ⁹Σ_g⁻	MRCI ^b	2525.263 135	2.18062	290.52	1.632	24.0	0.0
	MRCI ^c	2525.280 396	2.177 80	307.87	2.397	36.02	0.0
	C-MRCI ^b	2526.007 819	2.177 92	283.51	7.048		0.0
	MRCI-F12 ^d	2525.273 856	2.178 90	291.87	1.943	26.0	0.0
	C-MRCI-F12 ^d	2526.051 309	2.175 90	285.77	4.983		0.0
	MRCI-F12 ^e	2525.277 108	2.17865	294.51	2.780	26.1	0.0
	C-MRCI-F12e	2526.065 259	2.17412	284.81	4.681		0.0
	MRCI-DK ^f	2543.028 594	2.161 53	304.51	1.730	26.6	0.0
	C-MRCI-DK ^f	2543.773681	2.15984	292.68	1.083		0.0
	MRCI-F12-DK ^g	2543.038773	2.16012	298.28	-1.301	28.6	0.0
	C-MRCI-F12-DK ^g	2543.816080	2.16023	289.62	1.570		0.0
	MRCI-F12-DK ^h	2543.042694	2.15918	315.18	6.662	28.6	0.0
	C-MRCI-F12-DKh	2543.831014	2.154 58	308.31	8.611		0.0
	MRCI+Q ^b	2525.327 875	2.18277	312.79	6.430	33.7	0.0
	MRCI+Q ^c	2525.354 271	2.18434	318.73	-0.552	49.7	0.0
	C-MRCI+Q ^b	2526.166 851	2.165 19	300.84	2.525		0.0
	MRCI-F12+Q ^d	2525.339812	2.181 09	303.06	1.511	36.4	0.0
	C-MRCI-F12+Q ^d	2526.216231	2.16214	300.36	1.640		0.0
	MRCI-F12+Q ^e	2525.343 249	2.18083	303.89	1.612	36.5	0.0
	C-MRCI-F12+Q ^e	2526.230 528	2.161 17	301.04	-1.973		0.0
	MRCI-DK+Q ^f	2543.094 585	2.16346	314.97	1.404	38.5	0.0
	C-MRCI-DK+Q ^f	2543.934079	2.14647	317.84	3.883		0.0
	MRCI-F12-DK+Q ^g	2543.105965	2.163 94	308.18	-2.881	39.4	0.0
	C-MRCI-F12-DK+Q ^g	2543.982221	2.14472	289.62	-4.461		0.0
	MRCI-F12-DK+Q ^h	2543.110120	2.161 58	323.99	5.915	39.4	0.0
	C-MRCI-F12-DK+Qh	2543.997 620	2.14239	332.49	13.15		0.0
	AQCC ^b	2525.327 239	2.201 06	293.08	-0.430		0.0
	C-AQCC ^b	2526.195 867	2.188 14	296.95	0.760		0.0
	RCCSD(T) ^b	2525.346765	2.12935	345.88	1.155	28.0	0.0
	C-RCCSD(T) ^b	2526.251 097	2.113 38	353.08	1.211	28.7	0.0
	RCCSD(T)-F12be	2525.361 866	2.12976	346.59	1.244		0.0
	C-RCCSD(T)-F12be	2526.306084	2.111 50	354.68	1.583		0.0
	AQCC-DK ^f	2543.094142	2.183 18	305.64	4.891		0.0
	C-AQCC-DK ^f	2543.963 843	2.170 56	309.69	1.005		0.0
	RCCSD(T)-DK ^f	2543.115451	2.11670	356.33	0.442		0.0
	C-RCCSD(T)-DK ^f	2544.020846	2.101 01	363.65	1.083		0.0
$2^7 \Sigma_u^-$	MRCI ^b	2525.245 800	2.268 47	221.79	3.975	13.1	10.88
	MRCI+Q ^b	2525.310949	2.25520	263.69	-6.138	23.1	10.62
	MRCI-F12 ⁱ	2525.258 023	2.26444	260.00	2.015	16.1	12.0
	MRCI-F12+Q ⁱ	2525.325773	2.249 33			27.6	8.8

 ${}^{a}D_{e}$ values calculated by using the atomic energies of Table IS and a mean size-extensivity error of 0.036714(0.016409) E_{h} and 0.039107(0.019409) E_{h} for the MRCI(+Q) and MRCI-F12(+Q) results, respectively.

^bState specific calculations with the cc-pwCVQZ-NR basis set.

^cAugmented state specific calculations with the cc-pwCVQZ-NR basis set, for details see text.

^dState specific explicitly correlated calculations with the aug-cc-pwCVTZ-NR (AO basis set)/aug-cc-pwCVTZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-TZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets. ^eState specific explicitly correlated calculations with the aug-cc-pwCVQZ-NR (AO basis set)/aug-cc-pVQZ-NR MP2 fitting

(DF and RI basis sets) (Ref. 35)/DEF2–QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets. ^f State specific calculations with the cc-pwCVQZ–DK basis set.

^gState specific explicitly correlated calculations with the aug-cc-pwCVTZ-DK (AO basis set)/aug-cc-pwCVTZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-TZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets. ^hState specific explicitly correlated calculations with the aug-cc-pwCVQZ-DK (AO basis set)/aug-cc-pVQZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets. ⁱ State specific explicitly correlated calculations with the aug-cc-pVQZ-NR (AO basis set)/aug-cc-pVQZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets.

the $D_e = 45.8$ kcal/mol binding energy obtained through the $\omega_e^2/4\omega_e x_e$ formula, providing in essence the "true" diabatic "horse power" of this state. It is in perfect agreement with the diabatic $D_e(= 46.35 \text{ kcal/mol})$ given out explicitly in

Ref. 42 and with our augmented MRCI+Q D_e value of 49.67 kcal/mol.

Our first excited state is of ${}^{7}\Sigma_{u}^{-}$ symmetry with a T_e value of 11.79 kcal/mol at the state averaged MRCI+Q/cc-pVQZ

TABLE III. Energies $E(E_h)$, bond distances $r_e(Å)$, harmonic frequencies $\omega_e(cm^{-1})$, anharmonic corrections $\omega_e x_e(cm^{-1})$, adiabatic dissociation energies $D_e(kcal/mol)$ and electron affinities (EA)/ionization energies (IE) (eV) of the $X^8 \Sigma_u^{-(56} Fe_2^-)$, and $X^8 \Sigma_u^{-(56} Fe_2^+)$ states at different levels of theory, experimental results in square brackets.

Method	-E	r _e	ω _e	$\omega_e \mathbf{x}_e$	D_e	EA/IE
			$\operatorname{Fe}_{2}^{-}(X {}^{8}\Sigma_{\mu}^{-})$			
MRCI-F12 ^a	2525.276 694	2.208 09	281.29	1.256	48.55	0.18
MRCI-F12+Q ^a	2525.358 136	2.250 43	259.55	1.559	35.35	0.55
MRCI-F12 ^b	2525.277 829	2.213 59	244.69	1.898	38.35	0.07
MRCI-F12+Q ^b	2525.352 203	2.330 29	254.12	-0.532	37.91	0.29
MRCI-F12 ^c	2525.276368	2.212 52			38.48	0.07
MRCI-F12+Q ^c	2525.350 572	2.327 65	256.31	1.844	36.53	0.29
C-MRCI-F12 ^c	2526.044 837	2.18936	284.74	4.389	38.16	-0.18
C-MRCI-F12+Q ^c	2526.220113	2.201 31	278.68	1.331	41.41	0.11
RCCSD(T)-F12bd	2525.354759	2.175 67	317.56	1.201	21.21	-0.19
C-RCCSD(T)-F12bd	2526.303 350	2.143 81	335.03	1.121	19.69	-0.07
		$[2.10 \pm 0.04]^{e}$	$[250 \pm 20]^{e}$		$[35.28 \pm 3.92]^{e}$	$[0.902 \pm 0.008]^{e}$
					$[43.82 \pm 2.08]^{f}$	
			$\operatorname{Fe}_{2}^{+}(X \ ^{8}\Sigma_{u}^{-})$			
MRCI-F12 ^a	2525.067 542	2.168 08	296.15	0.951	40.72	5.51
MRCI-F12+Q ^a	2525.125979	2.168 89	309.56	2.833	53.85	5.76
MRCI-F12 ^b	2525.078774	2.17013	302.57	3.924	39.80	5.35
MRCI-F12+Q ^b	2525.130848	2.164 39	312.73	1.816	52.26	5.73
RCCSD(T)-F12bd	2525.135 182	2.09649	368.99	1.307	63.88	6.17
C-RCCSD(T)-F12bd	2526.078 167	2.078 83	377.83	1.117	64.39	6.20
					$[62.73 \pm 1.61]^{f}$	$[6.30 \pm 0.01]^{g}$
					$[63.19 \pm 2.31]^{h}$	

^aState averaged explicitly correlated calculations for the ground states of the species Fe_2^{-+} with the aug-cc-pVQZ-NR (AO basis set)/aug-cc-pVQZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets.

^bState specific explicitly correlated calculations for the ground states of the species Fe_2^{-+} with the aug-cc-pVQZ-NR (AO basis set)/aug-cc-pVQZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets.

^cState specific valence and core-valence (C-) explicitly correlated calculations for the ground state of the species Fe_2^- with the aug-cc-pwCVTZ-NR (AO basis set)/aug-cc-pwCVTZ-NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2-TZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets.

^dState specific valence and core–valence (C-) explicitly correlated calculations for the ground state of the species Fe_2^{-+} with the aug–cc–pwCVQZ–NR (AO basis set)/aug–cc–pVQZ–NR MP2 fitting (DF and RI basis sets) (Ref. 35)/DEF2–QZVPP (density fitting basis for Fock and exchange matrices) (Ref. 36) basis sets.

^eReference 10. ^fReference 42.

^gReference 44.

^hReference 43.

level of theory (Table I). Although this T_e value is very close to the experimental 12.31 ± 0.09 kcal/mol one,¹⁰ this is not a state that can be reached from $X^{8}\Sigma_{u}^{-}(Fe_{2}^{-})$ through a one photon experiment by detaching a σ_{u} electron. The next lying state that can indeed be the one observed in the negative ion photoelectron spectroscopy is the $3^{7}\Sigma_{g}^{-}$ one, lying just 13.80 kcal/mol above the ground state (Table I). The

 $2^{7}\Sigma_{u}^{-}$ PEC dissociates adiabatically to the mixed asymptote but the $3^{7}\Sigma_{g}^{-}$ PEC to the ground asymptotic channel due to a severe avoided crossing (Figs. 6 and 7S³⁴ for a more detailed view of all $^{7}\Sigma_{g}^{-}$ states involved in the avoided crossing).

The $2^{7}\Sigma_{u}^{-}$ and $3^{7}\Sigma_{g}^{-}$ states are of multi configurational character as reflected in their equilibrium configurations

$$\begin{split} |2^{7}\Sigma_{u}^{-}\rangle &\cong \left|1\sigma_{g}^{+2}2\sigma_{g}^{+2}[(0.53)1\delta_{g}^{2} - (0.29)1\delta_{u}^{2}]1\pi_{u,x}^{2}1\pi_{u,y}^{2}1\delta_{g}^{1}1\sigma_{u}^{+}2\sigma_{u}^{+}1\pi_{g,x}^{1}1\pi_{g,y}^{1}1\delta_{u}^{1}\right\rangle \\ &+ \left|1\sigma_{g}^{+2}2\sigma_{g}^{+2}1\delta_{g}^{1}1\pi_{u,x}^{2}1\pi_{u,y}^{2}[(0.53)1\delta_{g}^{2} - (0.29)1\delta_{u}^{2}]1\sigma_{u}^{+}2\sigma_{u}^{+}1\delta_{u}^{1}1\pi_{g,x}^{1}1\pi_{g,y}^{1}\right\rangle \end{split}$$

and

$$\begin{split} \left| 3^{7} \Sigma_{g}^{-} \right\rangle &\cong 0.52 \left| 1 \sigma_{g}^{+2} 2 \sigma_{g}^{+2} 1 \delta_{g}^{1} 1 \pi_{u,x}^{2} 1 \pi_{u,y}^{2} 1 \delta_{g}^{1} 1 \sigma_{u}^{+2} 1 \delta_{u}^{1} 1 \pi_{g,x}^{1} 1 \pi_{g,y}^{1} 1 \delta_{u}^{1} \right\rangle \\ &\quad + 0.25 \left[\left| 1 \sigma_{g}^{+2} 2 \sigma_{g}^{+} 1 \delta_{g}^{2} 1 \pi_{u,x}^{2} 1 \pi_{u,y}^{2} 1 \delta_{g}^{1} 1 \sigma_{u}^{+2} 2 \sigma_{u}^{+} 1 \pi_{g,x}^{1} 1 \pi_{g,y}^{1} 1 \delta_{u}^{1} \right\rangle \\ &\quad - \left| 1 \sigma_{g}^{+2} 2 \sigma_{g}^{+} 1 \delta_{g}^{1} 1 \pi_{u,x}^{2} 1 \pi_{u,y}^{2} 1 \delta_{g}^{2} 1 \sigma_{u}^{+2} 2 \sigma_{u}^{+} 1 \delta_{u}^{1} 1 \pi_{g,x}^{1} 1 \pi_{g,y}^{1} \right\rangle \right]. \end{split}$$

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FIG. 1. MRCI/cc-pVQZ PECs of all ⁹Λ Fe₂ states.

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FIG. 3. MRCI/cc–pVQZ PECs of all ${}^5\Lambda\,Fe_2$ states. The lowest bound state $({}^5\Delta_u)$ is in red.



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FIG. 5. MRCI/cc–pVQZ PECs of all ${}^{1}\Lambda$ Fe₂ states. The lowest bound state $({}^{1}\Sigma_{u}^{-})$ is in red.

The $3 {}^{7}\Sigma_{g}^{-}$ PEC minimum, with a barrier to dissociation of about 890 cm⁻¹, is due to the electrostatic interaction between the repulsive part of the vdW PEC and the last ${}^{7}\Sigma_{g}^{-}$ state dissociating to the mixed asymptote via the three intervening ${}^{7}\Sigma_{g}^{-}$ states, see Fig. 7S.³⁴

The two remaining and practically degenerate ${}^{7}\Delta_{g}/{}^{7}\Delta_{u}$ states (Fig. 6) owe their very shallow potential minima to the very sharp avoided crossings between a vdW PEC and a truly bound state coming from the mixed asymptote; see Fig. 7S for the ${}^{7}\Delta_{g}$ state and Fig. 9S for its ${}^{7}\Delta_{u}$ companion.

In addition to the above mentioned states, there is a cluster of ~20 states lying some 4400 cm⁻¹ above the $X \,{}^{9}\Sigma_{g}^{-}$, *i.e.*, ${}^{9}\Sigma_{g}^{-}$ (Fig. 1S), ${}^{9}\Gamma_{u}$ and ${}^{9}\Sigma_{u}^{+}$ (Fig. 3S), ${}^{9}\Phi_{g}$, ${}^{9}\Pi_{g}$, and ${}^{9}H_{g}$ (Fig. 4S), ${}^{7}\Gamma_{g}$ (Fig. 7S), ${}^{7}H_{u}$ (Fig. 8S), ${}^{7}\Sigma_{g}^{+}$ (Fig. 12S), ${}^{5}\Sigma_{u}^{+}$ and ${}^{5}\Gamma_{u}$ (Fig. 15S), and ${}^{3}\Delta_{g}$ (Fig. 19S).

Due to the plethora of states and the morphology of their PECs, which causes most of the vibrational levels to predissociate, it is not useful to discuss the calculated results in further detail. The present study unveils the tremendous complexity of Fe₂ that is perhaps the reason behind the scarcity and incompleteness of the experimental information.



FIG. 6. MRCI/cc–pVQZ PECs of the $X \,{}^{9}\Sigma_{g}^{-}, 2^{7}\Sigma_{u}^{-}, 3^{7}\Sigma_{g}^{-}, {}^{7}\Delta_{g}/{}^{7}\Delta_{u}$ states. The asymptotic channels are displaced to the experimental $\Delta E({}^{5}F \leftarrow {}^{5}D)$ energy gap.

B. Fe₂⁺ and Fe₂⁻

For reasons of completeness, we have also studied the ground states of the charged species Fe_2^- and Fe_2^+ . We have considered as such the ${}^8\Sigma_u^-$ symmetry (see Ref. 19) for both species, since we have not performed a detailed study, as in the case of neutral Fe₂.^{45,46}

The only experimental study of Fe₂⁻ is by Leopold and Lineberger¹⁰ and Leopold *et al.*,¹¹ who established a vibrational frequency of 250 ± 20 cm⁻¹, a bond length of 2.10 ± 0.04 Å, a bond strength of 1.53 ± 0.17 eV, and an EA = 0.902 ± 0.08 eV. The cationic species has been studied by the Armentrout group^{42,43} in collision induced experiments and determined its D^o = 2.74 ± 0.10 eV.⁴³

We have studied their ground states with a variety of methods/basis sets (see Table III). Their main CASSCF configurations are

$$X^{8}\Sigma_{u}^{-}(\text{Fe}_{2}^{-})\rangle \approx 0.88 \left| 1\sigma_{g}^{+2}2\sigma_{g}^{+2}1\delta_{g}^{1}1\pi_{u,x}^{2}1\pi_{u,y}^{2}1\delta_{g}^{1}1\sigma_{u}^{+2}2\sigma_{u}^{+1}1\delta_{u}^{1}1\pi_{g,x}^{1}1\pi_{g,y}^{1}1\delta_{u}^{1} \right|$$

and

$|X^{8}\Sigma_{u}^{-}(\mathrm{Fe}_{2}^{+})\rangle \approx 0.85 |1\sigma_{g}^{+2}2\sigma_{g}^{+2}1\delta_{g}^{1}1\pi_{u,x}^{2}1\pi_{u,y}^{2}1\delta_{g}^{1}1\sigma_{u}^{+1}1\delta_{u}^{1}1\pi_{g,x}^{1}1\pi_{g,y}^{1}1\delta_{u}^{1}\rangle.$

Comparing the above with those of the $X^{9}\Sigma_{g}^{-}(Fe_{2})$ we see that the anion is formed by the addition of a σ_{u}^{+} electron while the cation originates when a σ_{u}^{+} electron is extracted. This is in line with the simple interpretation of the Fe₂⁻ photoelectron spectra by Leopold *et al.*,¹¹ as well as with the theoretical studies of HS¹⁵ and Hoyer *et al.*¹⁹

Generally speaking, the numerical data obtained in the present study are in good agreement with the available experiments.

IV. CONCLUSIONS

We have studied a plethora (175) of Fe₂ states dissociating to the ⁵D + ⁵D and ⁵D + ⁵F asymptotes by multireference methods, while the ground $X^{9}\Sigma_{g}^{-}$ state has been painstakingly considered by a multitude of methods/basis sets. All states originating from the ground dissociation channel are of vdW type and thus of decreased chemical interest but their repulsive parts cut or interact strongly with the bound states that stem from the first excited channel causing their vibrational levels to predissociate.

The $X {}^{9}\Sigma_{g}^{-}$ lies below the ${}^{5}D + {}^{5}D$ level at the augmented MRCI+Q level of theory by at least 29 kcal/mol. The complexity of the system is in the very heart of both experimental and theoretical problems encountered so far and the present study provides a road map for a more sophisticated and focused work on this perplexing but fascinating molecule.

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- ¹S.-S. Lin and A. Kant, J. Phys. Chem. 73, 2450 (1969).
- ²T. C. de Vore, A. Ewing, H. F. Franzen, and V. Calder, Chem. Phys. Lett. **35**, 78 (1975).
- ³P. A. Montano, P. H. Barrett, and Z. Shanfield, J. Chem. Phys. **64**, 2896 (1975).
- ⁴M. Moskovits and D. P. diLella, J. Chem. Phys. 73, 4917 (1980).
- ⁵H. Purdum, P. A. Montano, G. K. Shenoy, and T. Morrison, Phys. Rev. B 25, 4412 (1982).
- ⁶P. A. Montano and G. K. Shenoy, Solid State Commun. 35, 53 (1980).
- ⁷I. Shim and K. A. Gingerich, J. Chem. Phys. **77**, 2490 (1982).
- ⁸H. M. Nagarathna, P. A. Montano, and V. M. Naik, J. Am. Chem. Soc. **105**, 2938 (1983).
- ⁹C. A. Baumann, R. J. Van Zee, and W. Weltner, Jr., J. Phys. Chem. **88**, 1815 (1984).
- ¹⁰D. G. Leopold and W. C. Lineberger, J. Chem. Phys. 85, 51 (1986).
- ¹¹D. G. Leopold, J. Almlöf, W. C. Lineberger, and P. R. Taylor, J. Chem. Phys. 88, 3780 (1988).
- ¹²M. Tomonari and H. Tatewaki, J. Chem. Phys. 88, 1828 (1988).
- ¹³T. Noro, C. Ballard, M. H. Palmer, and H. Tatewaki, J. Chem. Phys. **100**, 452 (1994).
- ¹⁴C. W. Bauschlicher, Jr. and A. Ricca, Mol. Phys. 101, 93 (2003).
- ¹⁵O. Hübner and J. Sauer, Chem. Phys. Lett. **358**, 442 (2002).
- ¹⁶Reference 14 was accepted for publication on 17 January 2012 before Ref. 15 was even received by the editorial office of Chem. Phys. Lett. (10 April 2012). Unfortunately, and due to the special nature of the particular

issue of Mol. Phys., Ref. 14 was finally published in 2003 while Ref. 15 in 2002 without the authors of either papers knowing of the existence of the others' contribution.

- ¹⁷M. Casula, M. Marchi, S. Azadi, and S. Sorella, Chem. Phys. Lett. **477**, 255 (2009).
- ¹⁸C. Angeli and R. Cimiraglia, Mol. Phys. 109, 1503 (2011).
- ¹⁹C. E. Hoyer, G. Li Manni, D. G. Truhlar, and L. Gagliardi, J. Chem. Phys. 141, 204309 (2014).
- ²⁰A. Kalemos, I. G. Kaplan, and A. Mavridis, J. Chem. Phys. **132**, 024309 (2010).
- ²¹A. Kalemos and A. Mavridis, J. Chem. Phys. **135**, 134302 (2011).
- ²²O. Krechkivska, M. D. Morse, A. Kalemos, and A. Mavridis, J. Chem. Phys. 137, 054302 (2012).
- ²³A. Kalemos and A. Mavridis, Theor. Chim. Acta 132, 1408 (2013).
- ²⁴D. Tzeli, U. Miranda, I. G. Kaplan, and A. Mavridis, J. Chem. Phys. **129**, 154310 (2008).
- ²⁵H.-J. Werner and P. J. Knowles, J. Chem. Phys. **89**, 5803 (1988); P. J. Knowles and H.-J. Werner, Chem. Phys. Lett. **145**, 514 (1988); K. R. Shamasundar, G. Knizia, and H.-J. Werner, J. Chem. Phys. **135**, 054101 (2011).
- ²⁶T. Shiozaki, G. Knizia, and H.-J. Werner, J. Chem. Phys. **134**, 034113 (2011).
- ²⁷H.-J. Werner and P. J. Knowles, Theor. Chim. Acta **78**, 175 (1990); See also, P. G. Szalay and R. J. Bartlett, Chem. Phys. Lett. **214**, 481 (1993).
- ²⁸K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head–Gordon, Chem. Phys. Lett. **157**, 479 (1989); J. D. Watts, J. Gauss, and R. J. Bartlett, J. Chem. Phys. **98**, 8718 (1993); P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993); **112**, 3106 (2000).
- ²⁹T. B. Adler, G. Knizia, and H.-J. Werner, J. Chem. Phys. **127**, 221106 (2007); H.-J. Werner, G. Knizia, and F. R. Manby, Mol. Phys. **109**, 407 (2011); T. B. Adler, F. R. Manby, and H.-J. Werner, J. Chem. Phys. **130**, 054106 (2009); *ibid.* **130**, 241101 (2009).
- ³⁰M. Douglas and N. M. Kroll, Ann. Phys. **82**, 89 (1974); B. A. Hess, Phys. Rev. A **32**, 756 (1985); **33**, 3742 (1986); M. Reiher and A. Wolf, J. Chem. Phys. **121**, 2037 (2004).
- ³¹T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
- ³²N. B. Balabanov and K. A. Peterson, J. Chem. Phys. 123, 064107 (2005).
- ³³H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2012.1, a package of *ab initio* programs, 2012, see http://www.molpro.net.
- ³⁴See supplementary material at http://dx.doi.org/10.1063/1.4922793 for the atomic energies (Table IS) and for all PECs (Figs. 1S–30S) of the Fe₂ system.
- ³⁵D. H. Bross, J. G. Hill, H.-J. Werner, and K. A. Peterson, J. Chem. Phys. 139, 094302 (2013).
- ³⁶F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys. 7, 3297 (2005).
- ³⁷A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, NIST Atomic Spectra Database (ver. 5.2), National Institute of Standards and Technology, Gaithersburg, MD, 2014, available online: http://physics.nist.gov/asd [23 March 2015].
- ³⁸See, for example, in E. Clementi and A. Veillard, J.Chem. Phys. 44, 3050 (1966) and references therein. We should note that the description of two singly coupled electrons into two different spatial functions is due to W. Heisenberg as applied in the He(¹S) case [W. Heisenberg, Z. Phys. 38, 411 (1926)]. The same idea has been worked out formally by W. Goddard III and J. Gerratt.
- ³⁹In Ref. 19, the ${}^9\Sigma_{g}^-$, ${}^7\Sigma_{g}^-$, and ${}^7\Delta_{tt}$ states do not have the same computational needs with respect to their active space composition.
- ⁴⁰C. F. Bunge, J. A. Barrientos, and A. V. Bunge, At. Data Nucl. Data Tables **53**, 113 (1993).
- ⁴¹T. L. Haslett, M. Moskovits, and A. L. Weitzman, J. Mol. Spectrosc. 135, 259 (1989).
- ⁴²S. K. Loh, L. Lian, D. A. Hales, and P. B. Armentrout, J. Phys. Chem. 92, 4009 (1988).
- ⁴³L. Lian, C.-X. Su, and P. B. Armentrout, J. Chem. Phys. 97, 4072 (1992).
- ⁴⁴E. A. Rohlfing, D. M. Cox, A. Kaldor, and K. H. Johnson, J. Chem. Phys. 81, 3846 (1984).
- 45 In a recent RCCSD(T) study of Fe₂⁺ (see Ref. 46), a $^{10}\Sigma_g^-$ symmetry was suggested for its ground state.
- ⁴⁶A. Irigoras, M. del Carmen Michelini, E. Sicilia, N. Russo, J. M. Mercero, and J. M. Ugalde, Chem. Phys. Lett. **376**, 310 (2003).