# Ab Initio Calculation of Inner-Sphere Reorganization Energies of Inorganic Redox Couples

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**Abstract:** Values of the inner-sphere reorganization energies ($\lambda_i$) for a number of small-molecule inorganic redox couples ($NO^+/NO$, $NO_2^+/NO_2$, $NO_2/NO_2^-$, $N_3/N_3^-$, $O_2/O_2^-$, $O_3/O_3^-$, $SO_2/SO_2^-$, $ClO/ClO^-$, $ClO_2/ClO_2^-$, and $Cl_2/Cl_2^-$) have been calculated by ab initio methods. The $\lambda_i$ values were calibrated by comparing calculated bond lengths/angles, electron affinities, and ionization potentials with experimental data and were found to be accurate to within ±2 kcal mol$^{-1}$ or better. Classically calculated $\lambda_i$ agreed well with the ab initio values, lending further credibility to previous conclusions regarding the electron-transfer chemistry of the redox species involved. In particular, the very high $\lambda_i$ of $NO_2^+/NO_2$ was reproduced by the ab initio calculations, thus explaining the low ET reactivity of nitronium ion toward organic compounds.

## Introduction

Reorganization energies, commonly denoted $\lambda$, are important parameters in the Marcus theory of outer-sphere electron transfer.[1,2] In simple terms, the reorganization energy represents the free energy increase associated with the structural changes of the reactants and their immediate environment which are necessary in order for the molecular system to proceed from the initial state to the transition state. The reorganization energy thus encompasses the changes in the nuclear coordinates of the reactants (bond or *i*nner-sphere reorganization energy, $\lambda_i$) and in the solvation shell (solvent or *o*uter-sphere reorganization energy, $\lambda_o$) which take place in proceeding from the initial state to the transition state. Reorganization energies can be determined either theoretically by calculation of the two contributing terms ($\lambda = \lambda_i + \lambda_o$), usually by classical methods based on simple force fields ($\lambda_i$) or the Born equation ($\lambda_o$), or experimentally by kinetic methods. In the latter case, one can measure electron-transfer rate constants of self-exchange reactions in solution [eq 1], the reorganization energy of which is often denoted $\lambda(0)$ to signify

$$\mathrm{A} + \mathrm{A}^- \overset{\Delta G^*(0) = \lambda(0)/4}{\rightleftharpoons} \mathrm{A}^- + \mathrm{A} \qquad (1)$$

that this type of reaction has $\Delta G^\circ = 0$. The $\lambda(0)$ value is then equal to $4\Delta G^*(0)$. Figure 1 illustrates these relationships for the self-exchange raction of eq 1. The left parabola symbolizes the potential surface of the reactants and the right one that of the products. The transition state is represented by the intersection point of the forbidden crossing of the parabolas and its height above the energy levels of the initial/final states is equal to $\lambda(0)/4 = \Delta G^*(0)$.

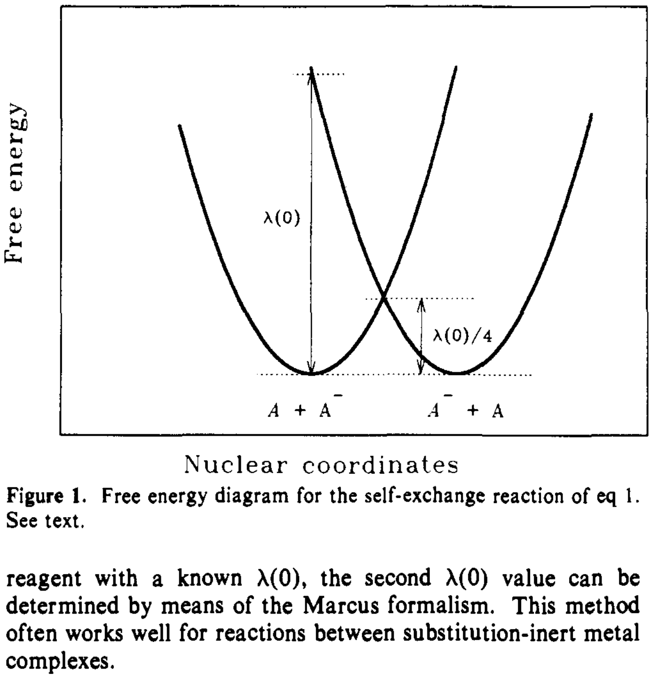

Figure 1. Free energy diagram for the self-exchange reaction of eq 1. See text.

Furthermore, it is an approximation of the Marcus theory that $\lambda$ of a heteroexchange reaction is equal to the mean value of those of the two self-exchange reactions involved. If one can measure the electron-transfer rate constant of a heteroexchange reaction, where one of the reactants is a well-established outer-sphere reagent with a known $\lambda(0)$, the second $\lambda(0)$ value can be determined by means of the Marcus formalism. This method often works well for reactions between substitution-inert metal complexes.

Obviously, the kinetic method relies entirely on the assumption that the reaction is of the outer-sphere type, i.e., with a negligibly small electronic interaction, usually put at $\leq 1$ kcal mol$^{-1}$, between the reactants in the transition state. This cannot always be taken for granted, especially when covalent inorganic or organic species are involved. In a comparison between classically calculated and experimental $\lambda(0)$ of a large number of organic self-exchange reactions,[3] it was noticed that experimental $\lambda(0)$ often are significantly smaller than the calculated ones, even with the assumption that $\lambda_i(0)$ can be neglected, e.g., for delocalized systems.[4] Later, this was put on a semiquantitative theoretical basis by the Shaik-Pross configuration mixing (CM) model[5] and shown to be a problem of general nature for covalent compounds; it is more likely than not that the electron-transfer (ET) transition-

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**Table I.** Experimental Values of $\lambda(0)$ of $O_2/O_2^-$, as Obtained from ET Rate Constants of Heteroexchange with Various Oxidants[d]

| oxidant[a] | $\lambda(0)$ of $O_2/O_2^-$,[b] kcal mol$^{-1}$ | oxidant[a] | $\lambda(0)$ of $O_2/O_2^-$,[b] kcal mol$^{-1}$ |
|---|---|---|---|
| $Fe(CN)_6^{3-}$ | 103 | $Ru(NH_3)_6^{3+}$ | 57 |
| $Mo(CN)_8^{3-}$ | 99 | $Fe^{III}(edta)H_2O^-$ | 40 |
| $Fe(C_5H_5)_2^+$ | 83 | $Co(en)_3^{3+}$ | 29 |
| $Co(sep)^{3+}$ | 64 | quinones | 22–27 |
| $Ru(NH_3)_4(phen)^{3+}$ | 60 | $O_2/O_2^-$ | 46[c] |
| $Ru(NH_3)_5(isn)^{3+}$ | 56 | | |

[a] Phen = 1,10-phenanthroline, isn = isonicotinamide, sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.0]eicosane, edta = ethylenediaminetetraacetic acid. [b] Calculated from the self-exchange rate constant, $k_{ex}(0)$, by the Eyring equation: $\log k_{ex}(0) = 11 - \lambda(0)/(4 \times 2.303RT)$. [c] Reference 8. [d] Data were taken from a compilation in ref 7.

state possesses a sizable electronic interaction between the reactants. Thus inner-sphere ET should be more prevalent than is usually assumed.[6]

A notorius case of inorganic nature is the $\lambda(0)$ of $O_2/O_2^-$ for which $\lambda$ values in the range of 22–103 kcal mol$^{-1}$ have been determined by kinetic methods (Table I).[7] A direct determination of the self-exchange rate constant gave $\lambda(0) = 46$ kcal mol$^{-1}$.[8] Theoretically, the classical treatment[9] gave 60 kcal mol$^{-1}$, with $\lambda_i = 15$ and $\lambda_o = 45$ kcal mol$^{-1}$. Such a widely varying $\lambda(0)$ must partly be due to the fact that the small oxygen/superoxide species (and it may well be that the effective size is strongly dependent upon solvation)[7] easily can come close enough to the second reactant for significant electronic overlap to develop in the transition state. This is particularly relevant for the reaction between superoxide and quinones where an inner-sphere ET mechanism should be favored by the electronic properties of both components.

A case showing the large difference in this respect even for closely related systems involves $NO^+/NO$ and $NO_2^+/NO_2$ where the experimental $\lambda(0)$ of the former system[10] is almost the same as the calculated one[11] (69 vs 70 kcal mol$^{-1}$), whereas for $NO_2^+/NO_2$ the experimental value is much smaller[12] than the theoretically calculated one[11] (60 vs 140 kcal mol$^{-1}$). This difference is reflected in the chemistry of these species; $NO^+$ is a typical one-electron-transfer oxidant[13] according to eq 2, whereas $NO_2^+$ is a typical electrophile [eq 3] in spite of its very high formal redox potential, $E°(NO_2^+/NO_2)$ being around 2 V vs NHE in various organic solvents.[12]

$$ArH + NO^+ \rightleftarrows ArH^{\bullet +} + NO \qquad (2)$$

$$ArH + NO_2^+ \rightarrow Ar(H)NO_2^+ \qquad (3)$$

In view of the difficulties in interpreting experimental $\lambda(0)$ data, it becomes important to establish reliable theoretical methods for estimates of the outer-sphere limiting $\lambda(0)$ values. The classical methods of estimating $\lambda_i(0)$ and $\lambda_o(0)$ are considered to be reliable, although they are based on simple approximations. However, one difficulty is to find values of the parameters required (force constants, bond lengths, and bond angles) that are accurate enough, especially for highly reactive species that are experimentally inaccessible. The sometimes remarkably high $\lambda$ values obtained by the classical method, as for the example that of $NO_2^+/NO_2$, has provoked scepticism in some quarters and therefore complementary and more reliable methods are needed. A new method for the calculation of $\lambda_i$, using analytical gradient and Hessian formalism was recently[14] applied to the benzyl$^\bullet$/benzyl$^-$ and butyl$^\bullet$/butyl$^-$ systems and was shown to be an improvement over the classical method. We now show that ab initio calculations of $\lambda_i$ for a number of covalent inorganic redox couples give results which should be more reliable than those calculated by classical methods. As it happens, the latter are in reasonably good agreement with the ab initio values for the redox couples chosen.

## Theoretical Calculations on Redox Couples

Ab initio quantum chemical methods have been used to compute the properties of a number of inorganic redox couples, listed in Table I. A full geometry optimization has been done for each component of the couples. The $\lambda_i$ values have been calculated by locating the minimum on the surface of the summed energies for the two redox components, and $\lambda_i$ was then obtained as $4(\Delta E_1 + \Delta E_2)$, where $\Delta E_i$ ($i = 1, 2$) is the energy needed to bring one of the components from the equilibrium geometry to the transition state. No assumption has been made about the shape of the potential curves, and the above relation is simply used as a definition of $\lambda_i$. In most cases a harmonic approximation would yield accurate results but not always. An obvious exception is $NO_2^+/NO_2$, where the neutral molecule is bent while the cation is linear.

The calculated $\lambda_i$ are estimated to be correct to at least 2 kcal mol$^{-1}$. A check of the accuracy can in most cases be obtained from computed geometries, electron affinities (EA), and ionization potentials (IP). Errors in the ET energies should be reflected by much larger errors in the absolute energy differences between the neutral and the ionic component of the redox couple. Below we will present these data together with data for the equilibrium geometries.

Most calculations have been performed using the coupled pair functional (CPF) approach of Ahlrichs et al.[15] The CPF method is known to give accurate results in cases where the wave function is dominated by a single configuration. This is the case for most systems studied. An exception was $O_3^-$, for which no stable geometry could be found by the CPF method, due to strong near degeneracy effects in the electronic structure. Here we used instead the complete active space (CAS) SCF method with dynamic correlation added using second-order perturbation theory.[17] This approach gives very accurate results for a number of properties of the ozone molecule, including geometrical parameters and vibrational frequencies.[18] The $O_2/O_2^-$ system was studied using CASSCF and multireference (MR) CI wave functions, since no accurate value for EA could be obtained by the CPF approach. The reason is that the EA of $O_2$ is negative at the Hartree–Fock level. As a result, the molecular orbitals become too diffuse, an error which cannot be corrected by the CPF approach.

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Contracted Gaussian basis sets of the ANO type were used.[19] For first-row elements the number of ANOs was 5s4p3d2f and for second-row elements 6s5p3d2f. Calculations were also performed with a smaller basis set (4s3p2d and 5s4p2d, respectively) in order to check the convergence of the results with the basis set. The results show that calculated $\lambda_i$ are converged to within a few tenth of a kcal mol$^{-1}$ with respect to a further increase in the AO basis set. The calculations were performed with the MOLCAS-2 quantum chemistry software.[20]

The resulting geometries and relative energies are presented in Table II together with experimental data. We will discuss these results briefly for each redox system, mainly to establish the accuracy of the computed $\lambda_i$ values. A more detailed account of the calculation of EAs for $O_2$ and $O_3$ will be given in separate publications,[21,31] in which the present results will also be related to earlier computational work.

**$NO/NO^+$.** The agreement between computed and experimental[22] bond distances is excellent and the same is true for the ionization energy.[23] The error in the calculated $\lambda_i$ in this case is ≤1 kcal mol$^{-1}$.

**$NO_2^+/NO_2/NO_2^-$.** The calculated geometries are again in full agreement with experimental data.[24–26] The computed IP is in error with ≈4 kcal mol$^{-1}$ [27] and the EA with 3 kcal mol$^{-1}$.[26] The geometries of the couple $NO_2/NO_2^-$ are similar, and the corresponding $\lambda_i$ can be expected to be accurate to within ±1 kcal mol$^{-1}$. The $NO_2^+/NO_2$ couple is different: while $NO_2$ is bent, $NO_2^+$ is linear. The transition state for ET is intermediate between these two geometries ($r = 1.165$ Å and $\Theta = 149.5°$). In order to establish the accuracy of the computed barrier, we have also calculated the energy to make $NO_2$ linear. No experimental value for this energy difference is known, but an extensive quantum chemical study exists[28] and gives the value 39.4 kcal mol$^{-1}$. The value obtained here is 40.2 kcal mol$^{-1}$. We thus conclude that the potential curves are well reproduced by the CPF approach used by us. From this evidence, together with the results given above, the calculated $\lambda_i$ can be estimated to have an error of not more than a few kcal mol$^{-1}$.

**$N_3/N_3^-$.** The computed $\lambda_i$ is close to zero. The extra electron in $N_3^-$ goes into a nonbonding orbital, resulting in an almost unchanged geometry compared to the neutral species. This compares well with experimental information,[29,30] which shows the bond distance in the ion to be only 0.006 Å longer than in $N_3$. Actually the CPF method gives a slightly unsymmetrical $N_3$ molecule with two different bond lengths. This is not in agreement with experiment.[30] A series of CASSF calculations was performed in order to obtain further information on this point. They resulted in a perfectly symmetrical structure ($D_{\infty h}$ symmetry). The symmetry lowering is thus an artefact of the CPF approach and was not further considered. In any case these consideration will not affect $\lambda_i$, since only small modifications of the bond distances were found.

**$O_2/O_2^-$.** The calculation of the electron affinity of the oxygen molecule turned out to be more difficult than for most other molecules of this study. It is the object of a separate investigation.[31] Here we will only give some preliminary results relevant for the calculation of $\lambda_i$. The CPF method was not considered appropriate for these studies, since the aim was to compute full potential curves. The basis set used in the preliminary studies was of the ANO type[19] and had the size 7s6p3d2f1g. CASSCF calculations were performed with the 2p orbitals active. Dynamic correlation was added using the MRCI approach with all the CAS configurations in the reference space. The EA obtained from this preliminary calculation was 6.5 kcal mol$^{-1}$ which is 4 kcal mol$^{-1}$ smaller than the experimental value (10.4 kcal mol$^{-1}$).[32] Dynamic correlation had a large effect on this value. The corresponding CASSCF result was −33.0 kcal mol$^{-1}$. As a result, there is a strong influence of dynamic electron correlation also on the electronic structure of $O_2^-$ which is difficult to describe. The best value obtained in our study was 9.0 kcal mol$^{-1}$ which is probably close to the full CI limit of the present basis set. The value was obtained by a systematic increase of the configuration space of the MRCI wave function.

However, small errors in the computed EA cancel to a large extent in the calculation of $\lambda_i$. The shape of the potential curves is more important. The bond distances given in Table I are slightly longer than the experimental ones.[22,32] The corresponding $\omega_e$ values are 1548 (1580) and 1107 (1073) cm$^{-1}$ for $O_2$ and $O_2^-$, respectively (experimental values[22,32] within parentheses). Judging from these data, we estimate that $\lambda_i$ is accurate within ±1 kcal mol$^{-1}$.

**$O_3/O_3^-$.** The $O_3/O_3^-$ system represents a true challenge to theory, since the wave function describes an intermediate between an ionic and a biradical structure. As a consequence there is considerable mixing of electronic configurations and single configurational approaches are thus not appropriate. Actually, the CPF method does not lead to a stable minimum for $O_3^-$. The CASSCF approach does not suffer from this problem since the configurational mixing is included already at the lowest level of theory. A second-order perturbation theory, recently developed,[17] has proved to give a good account of the remaining correlation effects for a number of properties of the ozone molecule,[18] including the force constants. This approach was therefore used in the present study. The CASSCF calculations had nine active orbitals (originating from the oxygen 2p orbitals). All electrons except 1s were correlated in the perturbation calculations.

The results, as presented in Table I, are in remarkably good agreement with experiment. The calculated EA differs only by 2 kcal mol$^{-1}$ from the measured one.[33,34] The same is true for the computed geometry of $O_3$ (experimental data from ref 35). The experimental geometry for $O_3^-$ has rather large errors,[34] and the theoretical data are here of higher quality. The computed $\lambda_i$ should be highly accurate.

The reason why ozone seems to be so much easier to describe theoretically than $O_3^-$ is the fact that the former is a bound species already at the level of CASSCF theory. Therefore the electronic structure is well described, and the remaining electron correlation effects can rather easily be accounted for. This is not the case for $O_2^-$, the electronic structure of which depends strongly on dynamic correlation effects.

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**$SO_2/SO_2^-$.** This system does not show the same near degeneracy effects as ozone. Therefore the CPF method could be safely used to compute $\lambda_i$ and the properties of the molecule and its negative ion. The calculated structures were in good agreement with experiment,[36,37] as was EA. The change in geometry after adding the electron to $SO_2$ is only modest and the corresponding $\lambda_i$ is small and should be well reproduced by the calculations.

**$ClO/ClO^-$ and $ClO_2/ClO_2^-$.** These systems do not present any problems for the theory. The CPF method gave reliable results. The computed bond distances were 0.01–0.02 Å longer than experimental ones,[38–41] but this is due to the limited basis set used here. The addition of g-type functions decreased the distances by 0.005–0.01 Å.[21] They had, however, only a minor effect on computed EAs which already at the present level were in good agreement with experimental data.[42] The lengthening of the bond distances with the addition of the extra electron was modest and well represented by theory.

**$Cl_2/Cl_2^-$.** A slightly larger ANO basis set was used for this system: 6s5p4d3f2g. Dissociation of both the neutral molecule and the ion was studied using both the CPF method and the CASSCF method plus second-order perturbation theory. The results for the equilibrium properties are rather similar, so that we report here only those obtained by the CPF method. The bond distance of $Cl_2$ was reported with an accuracy of 0.01 Å. $Cl_2^-$ has a much larger bond distance[43] and is best represented as a complex between a chlorine atom and $Cl^-$. The computed bond energy of the ion was 27 kcal mol$^{-1}$, about half the value for $Cl_2$. The calculated EA was within the error limits of the experiments.[44]

The large difference in geometry between $Cl_2$ and $Cl_2^-$ gives rise to a large $\lambda_i$, almost 73 kcal mol$^{-1}$. The errors in this value are somewhat uncertain since they depend on properties of the potential curves rather far from the equilibrium geometries. However, the computed dissociation energy of $Cl_2$ was 54.3 kcal mol$^{-1}$, in reasonable agreement with the experimental value, 58 kcal mol$^{-1}$.[22] Also the computed vibrational frequency ($\omega_e$), 561 cm$^{-1}$, agrees with the experimental value, 559 cm$^{-1}$. Considering this evidence, we estimate the accuracy of the computed $\lambda_i$ to be better than 2 kcal mol$^{-1}$.

Chen and Wentworth[43] have constructed Morse potential curves for the negative ion states of the halogens from experimental data. From their analysis the following spectroscopic constants were obtained: $r_e$ = 2.62 (2.59) Å, $\omega_e$ = 249 (261) cm$^{-1}$, $D_e$ = 31.8 (27.3) kcal mol$^{-1}$ and EA($Cl_2$) = 56.7 (54.3) kcal mol$^{-1}$ (our results within parentheses). The agreement is reasonable but not entirely consistent. One would expect a longer bond length and lower vibrational frequency to be associated with a smaller dissociation energy. This is not the case, which indicates some uncertainty in the analysis by Chen and Wentworth.

**Table II.** Calculated and Experimental Properties of the Components of Some Inorganic Redox Systems (Experimental Values within Parentheses)[a]

| system | $r_e$, Å | $\theta$, deg | EA,[b] kcal mol$^{-1}$ |
|---|---|---|---|
| $NO^+$ | 1.061 (1.063) | | 213.1 (213.5 ± 0.1) |
| $NO$ | 1.153 (1.151) | | |
| $NO_2^+$ | 1.117 (1.104) | 180 (180[c]) | 221.7 (224.8 ± 0.2) |
| $NO_2$ | 1.199 (1.194) | 133.4 (133.9) | 48.4 (52.4 ± 0.1) |
| $NO_2^-$ | 1.258 (1.25) | 116.5 (117.5) | |
| $N_3$ | 1.179 (1.182) | 180 (180) | 55.3 (61.8 ± 0.2) |
| $N_3^-$ | 1.182 (1.188) | 180 (180) | |
| $O_2$ | 1.219 (1.207) | | 9.0 (10.4 ± 0.2) |
| $O_2^-$ | 1.362 (1.347) | | |
| $O_3$ | 1.283 (1.278) | 116.7 (116.8) | 50.0 (48.5 ± 0.1) |
| $O_3^-$ | 1.361 (1.34) | 115.4 (113) | |
| $SO_2$ | 1.440 (1.431) | 118.8 (119.3) | 27.2 (25.5 ± 0.2) |
| $SO_2^-$ | 1.520 (1.52) | 113.7 (116) | |
| $ClO$ | 1.587 (1.570) | | 48.5 (52.5 ± 0.1) |
| $ClO^-$ | 1.702 (1.673) | | |
| $ClO_2$ | 1.484 (1.470) | 116.9 (117.4) | 49.7 (54.7 ± 0.2) |
| $ClO_2^-$ | 1.587 (1.59) | 113.2 (114) | |
| $Cl_2$ | 1.998 (1.988) | | 54.3 (55 ± 2) |
| $Cl_2^-$ | 2.59 (2.62) | | |

[a] References to experimental values are given in the text. [b] Adiabatic electron affinity in kcal mol$^{-1}$. [c] Reference 24 gives $\Theta_e$ = 175.2° for $NO_2^+$ from an X-ray crystallographic study, which presumably is a consequence of crystal packing. Like Quereshi et al.,[50] we favor the linear arrangement for the nitronium ion in solution.

**Table III.** Inner-Sphere Reorganization Energies ($\lambda_i$) of Inorganic Redox Couples, as Calculated by ab Initio or Classical Force-Field Methods

| couple | $\lambda_i$, kcal mol$^{-1}$ ab initio | $\lambda_i$, kcal mol$^{-1}$ classical | stretch/bend contribution, % | difference ab initio–classical, kcal mol$^{-1}$ |
|---|---|---|---|---|
| $NO^+/NO$ | 24.4 | 21.5 | | 2.9 |
| $NO_2/NO_2$ | 30.9 | 31.3 | 26/74 | –0.4 |
| $NO_2^+/NO_2$ | 106.7 | 97.1[a] | 8/92 | 11.7 |
| $NO_2^+/NO_2$ | 106.7 | 107.6[b] | 17/83 | –0.9 |
| $NO_2^+/NO_2$ | 106.7 | 124.8[c] | 29/71 | –18.1 |
| $N_3/N_3$ | 0.0 | ≈0 | | 0 |
| $O_2/O_2$ | 24.9 | 21.2 | | 3.7 |
| $O_3/O_3$ | 10.6 | 8.3 | 82/18 | 2.3 |
| $SO_2/SO_2$ | 16.1 | 19.4 | 97/3 | –3.3 |
| $ClO/ClO$ | 6.3 | 5.5 | | 0.8 |
| $ClO_2/ClO_2$ | 15.2 | 22.4 | 97/3 | –7.2 |
| $Cl_2/Cl_2$ | 72.8 | 74 | | –1.2 |

[a] $r_e$ = 1.154 Å. [b] $r_e$ = 1.129 Å. [c] $r_e$ = 1.154 Å.

## Discussion

Table III lists $\lambda_i$ calculated by ab initio and classical methods, together with the stretch/bend contributions to the classical $\lambda_i$. As noted above, the ab initio values are considered accurate to within ±2 kcal mol$^{-1}$ or better and thus represent a consistent series of $\lambda_i$, by which we can assess the accuracy of the classical values. It first must be noted that the results of the classical method often depend strongly on small differences between experimental quantities, such as bond lengths and bond angles, and therefore are subject to large errors. Secondly calculations for triatomic species with symmetrical transition states (in which both reactants have identical bond lengths and angles) have usually employed a simple valence force field,[11,45] assuming that the stretch–stretch ($f_{dd}$) and stretch–bend ($f_{d\alpha}/r_e$) interaction constants of the general valence force field[46] contribute negligibly to $\lambda_i$. This is not always the case, as pointed out by Bennett and Warlop[47] in connection with calculations of $\lambda_i$ for a number of triatomic species. They therefore included $f_{dd}$ in their calculations but not $f_{d\alpha}$, due to the fact that they mostly considered redox couples with $\lambda_i$ dominated by the bond stretching contribution, such as $O_3/O_3^-$, $ClO_2/ClO_2^-$, and $SO_2/SO_2^-$. The inclusion of $f_{d\alpha}$ for the calculation of $\lambda_i(NO_2/NO_2^-)$, a value dominated by bending contributions, was however omitted, presumably due to the "substantially more complex expression" for $\lambda_i$ which results when the $f_{d\alpha}$ contribution is considered in the general valence force field.

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**Table IV.** Force Constants Used in the Calculation of Classical $\lambda_i$

| species | $f_d$, mdyn Å$^{-1}$ | $f_{dd}$, mdyn Å$^{-1}$ | $f_\alpha r_e^{-2}$, mdyn Å$^{-1}$ | ref |
|---|---|---|---|---|
| $NO^+$ | 23.9 | | | 11a |
| NO | 15.9 | | | 51 |
| $NO_2$ | 7.5 | | 1.67 | 52 |
| $NO_2$ | 11.04 | 2.14 | 1.109 | 53 |
| $NO_2^+$ | 17.44 | 1.12 | 0.688 | 50 |
| $O_2$ | 11.4 | | | 47 |
| $O_2$ | 5.61 | | | 47 |
| $O_3$ | 5.70 | 1.52 | 1.28 | 47 |
| $O_3$ | 4.70 | 0.70 | 1.5 | 47 |
| $SO_2$ | 10.0 | 0.02 | 0.72 | 47 |
| $SO_2$ | 6.5 | 0.50 | 0.77 | 47 |
| ClO | 4.69 | | | 54[a] |
| $ClO^-$ | 2.84 | | | 42b[b] |
| $ClO_2$ | 6.82 | | 0.618 | 45 |
| $ClO_2$ | 4.25 | | 0.55 | 45 |
| $Cl_2$ | 3.3 | | | 43[b] |
| $Cl_2$ | 0.64 | | | 43[b] |

[a] Calculated from $\omega_e$ of $^{35}$ClO. [b] Calculated from the experimental $\omega_e$.

We noted the same difficulty and therefore restricted our calculations to the approximation introduced by Bennett and Warlop,[47] even for the couples where the bending contribution is predominant. In such situations, the classically calculated $\lambda_i$ represent minimum values. We used the experimental bond lengths and angles given in Table II for the calculations, together with the force constants listed in Table IV.

As seen in Table III and graphically expressed in Figure 2, the agreement between the two sets of $\lambda_i$ is remarkably good, the slope of the regression line of Figure 2 being 1.01 ± 0.03. The extremely large $\lambda_i(NO_2^+/NO_2)$ is well reproduced, also with the uncertainty of the bond length in $NO_2^+$ in mind. An older value[48] of 1.154 Å was later[24] replaced by 1.104 Å, and we have calculated $\lambda_i$ for both these values and their average. These results reinforce earlier proposals that it is the high reorganization energy of $NO_2^+/NO_2$ that makes $NO_2^+$ less well suited for ET oxidation and causes its electrophilicity to dominate its chemistry. Even if it is now recognized that $NO_2^+$ can oxidize aromatics by ET in some kind of inner-sphere mechanism,[13c] this large $\lambda_i$ must to some extent be felt also in any bonded transition state[49] preceding formation of the radical cation/$NO_2$ pair.

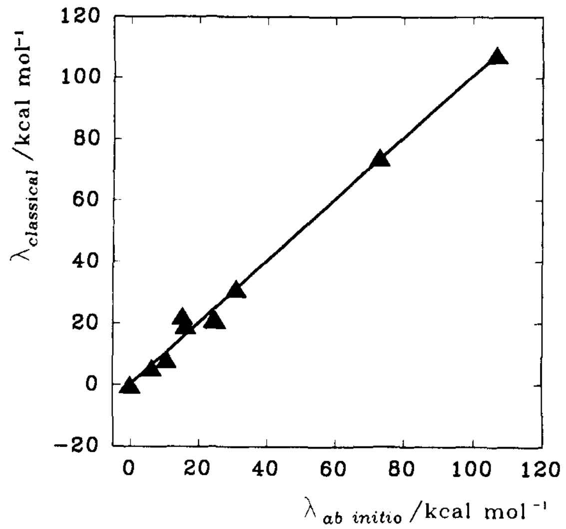

**Figure 2.** Plot of $\lambda_i$(classical) vs $\lambda_i$(ab initio); the slope of the regression line is 1.01 ± 0.03.

## Conclusions

Values of $\lambda_i$ can be calculated with good accuracy by ab initio methods, as shown by calibration of the calculations against experimental bond lengths/angles, EA and IP. Classically calculated $\lambda_i$ agree well with ab initio values, indicating that earlier conclusions regarding the chemistry of the redox couples still are valid.

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