

An *ab initio* study of the bonding in BeH ($X^2\Sigma^+$), BeH^- ($X^1\Sigma^+$), Be_2 ($X^1\Sigma_g^+$), O_3 (X^1A_1), and CO_3 ($\sim X^1A_1$) through an adiabatic to diabatic transformation

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An *ab initio* study of the bonding in BeH ($X^2\Sigma^+$), BeH⁻ ($X^1\Sigma^+$), Be₂($X^1\Sigma_g^+$), O₃ (\tilde{X}^1A_1), and CO₃ (\tilde{X}^1A_1) through an adiabatic to diabatic transformation

Apostolos KALEMOS

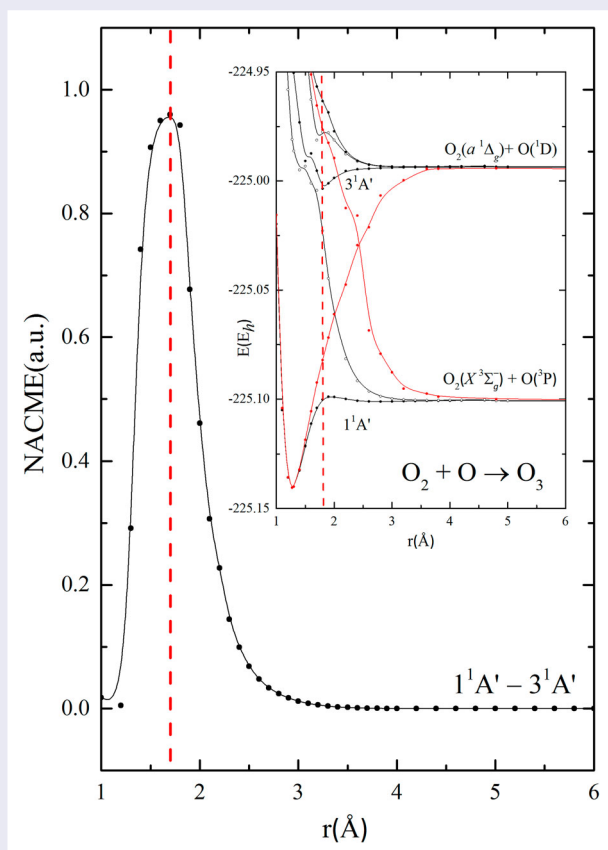
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ABSTRACT

We have studied the bonding situation in BeH ($X^2\Sigma^+$), BeH⁻ ($X^1\Sigma^+$), Be₂ ($X^1\Sigma_g^+$), O₃ (\tilde{X}^1A_1), and CO₃ (\tilde{X}^1A_1) both diabatically and adiabatically through MRCI calculations. In particular the Be containing species, BeH, BeH⁻ and Be₂, are formed through an excited ³P ($2s^12p^1$) Be state, the ground state O₃ molecule results from the interaction of the excited O₂ ($a^1\Delta_g$) + O (¹D) fragments and finally the CO₃ species results from the combination of CO ($a^3\Pi$) + 2 O (³P) / O₂ ($X^3\Sigma_g^-$).

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1. Introduction

Chemistry studies matter and its transformation at the atomic level. Its quantum mechanical theoretical description is greatly simplified by the introduction of the

Born – Oppenheimer (BO) approximation which fixes in space the various nuclei of the molecular species. This way the various classical concepts of chemistry survive in the quantum realm [1,2]. Under the BO mathematical

and computational scheme the atoms emerge as building blocks of the molecular species while the concept of the chemical bond acquires a legitimate quantum mechanical status. In order to understand its formation we usually need to spot it as a localized entity so we have to extract this ‘localized’ information from a rather complicated and delocalized molecular wavefunction.

A convenient starting point for such a task is a properly designed complete active space SCF (CASSCF) wavefunction. Several localization techniques have been proposed (see *e.g.* Refs. [3–5]) based on its invariance with respect to unitary transformations among the active orbitals. Ruedenberg and collaborators (see *e.g.* Ref. [6]) advanced the idea that free atoms partially survive in molecules and came up with the quasi atomic orbitals (QUAO) in order to rationalize the bonding formation and chemical transformations in reactions.

Another path towards the visual consideration of the chemical bond is through the spin coupled generalized valence bond (SCGVB) wavefunction [7,8]. It can be considered as the best single configuration representation of a CASSCF [9] but it has less variational degrees of freedom [10] so it is energetically inferior to a CASSCF. It nevertheless has some attractive features. The SCGVB orbitals sort out quasi localized and this is in line with the established chemical concepts while their evolution along a reaction path may be helpful in detailing the molecular formation process through an atoms – in – molecule (AIM) perspective [11].

Within the same AIM spirit Nicolaides and Komninos [12,13] presented an interesting theory that connects the molecular structure with the shape of the (usually excited) atomic state that is responsible for the molecular formation. This geometrically active atomic state is nevertheless not provided. Its knowledge results out of experience and trials. When correctly identified both the molecular shape and the corresponding hybridization result naturally by inspection of the maxima of the probability density.

But how can one identify this ‘correct’ atomic state? We have previously addressed this issue by constructing the non adiabatic coupling matrix elements (NACME) and corresponding diabatic curves [14–16] in a number of cases. And we intend to act similarly for BeH ($X^2\Sigma^+$), BeH[−] ($X^1\Sigma^+$), Be₂ ($X^1\Sigma_g^+$), O₃ (\tilde{X}^1A_1), and CO₃ (\tilde{X}^1A_1) with the goal to unveil the role of the excited atomic and/or fragmentary states in the formation of their respective ground molecular states.

2. Computational details

We have studied the formation of the titled species both diabatically and adiabatically through state averaged

CASSCF (SACASSCF) and multi reference CI (MRCI) calculations coupled with the (aug) – cc – pVQZ basis set. The technical details of the SACASSCF wavefunctions are as follow: SACASSCF (3e[−]/23 orb, 16 states) for BeH ($X^2\Sigma^+$); SACASSCF (4e[−]/23 orb, 16 states) for BeH[−] ($X^1\Sigma^+$); SACASSCF (4e[−]/26 orb, 6 states) for Be₂ ($X^1\Sigma_g^+$); SACASSCF (18e[−]/12 orb, 6 states) for O₃ (\tilde{X}^1A_1); and SACASSCF (16e[−]/13 orb, 16 states) for CO₃ (\tilde{X}^1A_1). The size of the active spaces and the number of states included in the SACASSCF calculations resulted after a number of trials. Diabatic curves have been constructed by rotating the adiabatic ones while the associated NACMEs have been computed by finite differences with a step of 0.01 Å along the chosen reaction path.

Diabatic curves have the property to retain the electronic characteristics of the asymptotic channel along the reaction path ($\langle \psi_i^{diabatic} | d/dQ_\kappa | \psi_j^{diabatic} \rangle = 0$) and consequently they are useful when an analysis of the chemical bond is in order. When two or more potential energy curves interact strongly, become degenerate or quasi degenerate the NACMEs acquire substantial values. The Born – Huang expansion [17] introduces the above couplings that arise from the nuclear kinetic energy operator acting on the electronic wavefunctions and contain 1st and 2nd order differential operators. This way the non adiabatic behavior is recovered but the singularities of the non adiabatic couplings create computational problems that are handled by transforming to a diabatic basis (see *e.g.* Refs. [18,19]) where the kinetic coupling is either minimized or completely eliminated. The transformation from an adiabatic to a diabatic basis is unitary and depends parametrically on $\langle \psi_i^{adiabatic} | d/dQ_\kappa | \psi_j^{adiabatic} \rangle$; see *e.g.* [20].

The MOLPRO computational package [21] has been employed throughout our work.

3. Results (past and present) and discussion

In what follows we shall present a critical survey of the existing literature related to the bonding description of the studied species. The most recent studies on BeH and BeH[−] are documented in Refs. [22–24] and [25–27], respectively, while both the neutral and anion species are discussed in Ref. [28]. Their bonding is only discussed in Refs. [22], [25], [27], and [28] and in the following we shall focus on their most important points.

In Ref. [22] we read.

‘... At short distances, let us say up to 3 Å, both MOs can be described as resulting from the bonding and non bonding ($2s_{\text{Be}} - 2p_{\text{Be}}$) hybrid + ($1s_{\text{H}}$).’

and

‘... The bond formation of BeH, both in the ground state (GS) and excited states, deserve special interest, as many other compounds of Be do, due to the relevance of the promotion from the $2s$ to the $2p$ orbital in the formation of the molecule.’

The BeH^- anion is studied in Ref. [25] but a discussion on its parental neutral species is also given. The authors state that

‘... it is well known that the Be atom is able to form two sp hybrid orbitals... placed in a linear arrangement at the opposite sides with respect to the Be atom... due to the quasi degenerate nature of the $2s$ and $2p$ atomic orbitals... Indeed, the first excited triplet state (^3P) is only 2.725192 eV above the ground state, ...’.

One of the above described sp hybrids combines with the $1s$ hydrogen orbital to form the σ BeH bond while the other (opposite) sp hybrid hosts the second Be valence electron and the minus charge. This bonding mode is condensed in the Lewis structure $(:\text{Be} - \text{H})^-$ and certainly this is in perfect agreement with the structure of the isoelectronic and linear $\text{H}:\text{Be} - \text{H}$ ($\leftarrow \text{H}^+ + (: \text{Be} - \text{H})^-$) system. All of the above ideas have been confirmed by carefully constructing FCI calculations. They have finally concluded that the bond formation is the result of two combined effects, the quasi degeneracy of the $2s$ and $2p$ orbitals and the very weak electron affinity of H.

In Ref. [27] the authors offer a comparative study of $\text{RG} - \text{H}^-$ ($\text{RG} = \text{He} - \text{Rn}$) and MH^- ($\text{M} = \text{Be} - \text{Ra}$). Based on QCISD contour plots and on an AIM population analysis the authors concluded that the bonding situation results from the displacement of the $2s^2$ Be density away from the incoming H^- ion into an sp hybrid and the partial donation of H^- into a dative covalent manner while both atoms retain the majority of their electron density (*i.e.*: $\text{Be} \leftarrow (\text{H}^-)$).

In Ref. [28] both BeH and BeH^- systems are discussed and the conclusions reached are in agreement with those in Ref. [25], *i.e.* the *in situ* Be atom is found in its excited ^3P state (stated explicitly), a covalent BeH bond is formed while the negative charge of BeH^- is coupled with the spin defining e^- of the neutral species in the sp hybrid opposing the BeH bond.

Concerning BeH (both neutral and anion) we have constructed adiabatic and diabatic potential curves at the MRCI level that show the excited nature of the *in situ* Be atom. The MRCI potential energy curves of six BeH states of $^2\Sigma^+$ symmetry are displayed in Figure 1. The NACMEs of the $X^2\Sigma^+ - 2^2\Sigma^+$ interaction are shown in Figure 2 along with the corresponding adiabatic and diabatic potential curves (see inset). The latter show the diabatic chemical origin of the ground $X^2\Sigma^+$ BeH minimum or in other words the excited *in situ* character ($2s^1 2p^1$; ^3P) of the Be atom. We should mention at

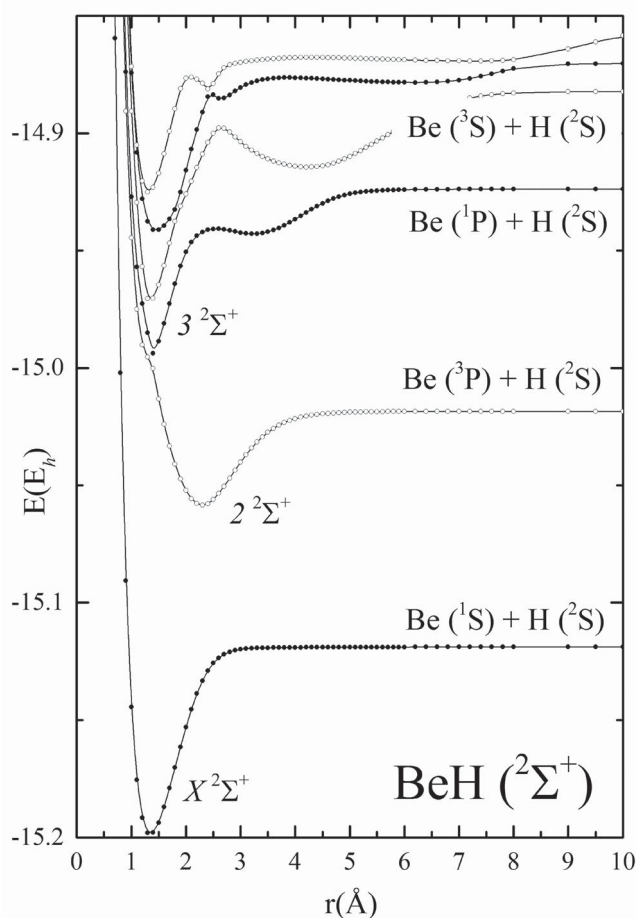


Figure 1. MRCI/aug-cc-pVQZ adiabatic potential energy curves of $\text{BeH} (^2\Sigma^+)$.

this point that the $X^2\Sigma^+ - 2^2\Sigma^+$ interaction/avoided crossing is mentioned in a SCGVB computationally study some forty years ago [29].

The formation of the anion appears to be straightforward. The additional electron is singlet coupled with the spin defining electron of the neutral species that resides in the sp hybrid opposing the BeH bond. The equilibrium CASSCF configuration is

$$|X^1\Sigma^+(^1A_1)_{C_{2v}}\rangle \cong 0.81|1a_1^2 2a_1^2\rangle - 0.46|1a_1^2 2a_1^1 4\bar{a}_1^1\rangle$$

where $1a_1$ ($\sim 0.65 [2s]_{\text{Be}} + 0.64 [1s]_{\text{H}}$) describes the covalent sigma BeH bond while $2a_1$ ($\sim 0.7 [2s]_{\text{Be}} - 0.5 [2p_z]_{\text{Be}} - 0.3 [1s]_{\text{H}}$) is a sp hybrid pointing away from the sigma bond. The 0.46 configuration describes the same situation as the 0.81 one but in a SCGVB way (a different orbital for different electrons).

Figure 3 shows the diabatic origin of its (BeH^-) equilibrium character. Its minimum relates adiabatically to the $\text{Be} (1\text{S}) + \text{H}^- (1\text{S})$ asymptote. Diabatically their interaction is repulsive as expected due to their closed shell character. The diabatic attractive interactions result not

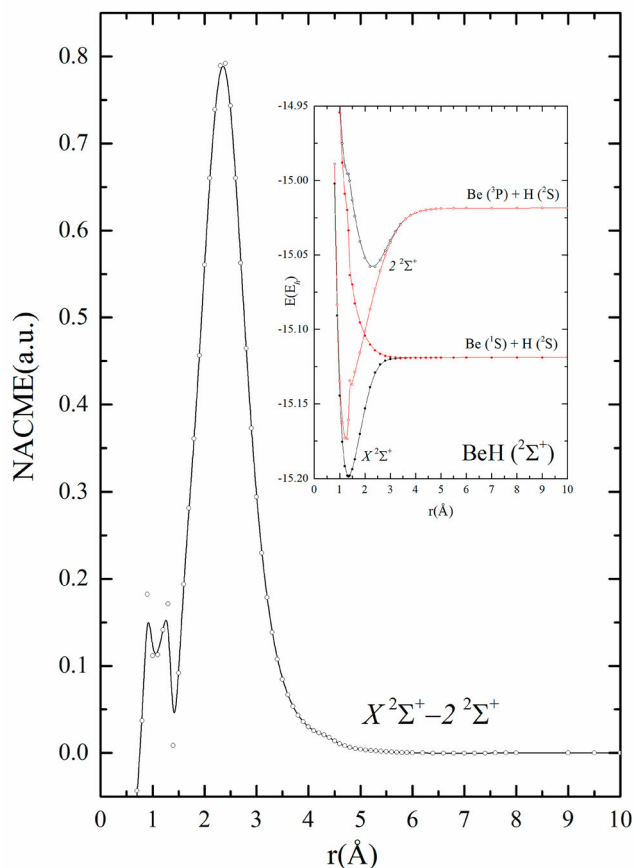


Figure 2. NACMEs of the BeH $X^2\Sigma^+ - 2^2\Sigma^+$ interaction along with their adiabatic (black curves) and diabatic (red curves) potential energy curves (inset). Numerical results at the MRCI/aug-cc-pVQZ computational level. Diabatization is treated as a 2×2 problem.

only from the $\text{Be}^- (^2P_{\text{Ryd}}) + \text{H}$ asymptote but also from higher Rydberg diabats (*i.e.* $\text{Be}^- (^2S_{\text{Ryd}})$, $\text{Be}^- (^2P_{\text{Ryd}})$; see Figure 3). The adiabatic curve, a ‘mixture’ of all these diabatic curves has an overall attractive character.

Although the ground Be state has a negative electron affinity this is not true for its first excited 3P ($2s^1 2p^1$) state. The following numerical MRCI results are quite indicative: $\Delta E(2s^1 2p^1; ^3P(\text{Be}) \leftarrow 2s^2; ^1S(\text{Be})) = 63.08$ kcal/mol but $\Delta E(2s^2 p^1; ^2P_{\text{Ryd}}(\text{Be}^-) \leftarrow 2s^2; ^1S(\text{Be})) = 6.91$ kcal/mol. For higher Rydberg states we have $\Delta E(2s^2 s^1; ^2S_{\text{Ryd}}(\text{Be}^-) \leftarrow 2s^2; ^1S(\text{Be})) = 16.90$ kcal/mol and $\Delta E(2s^2 p^1; ^2P_{\text{Ryd}}(\text{Be}^-) \leftarrow 2s^2; ^1S(\text{Be})) = 25.27$ kcal/mol. Thus $\text{Be}^- (2s^2 p^1; ^2P_{\text{Ryd}})$ is stabilized upon interaction with H and ‘lives’ inside $\text{BeH}^- (X^1\Sigma^+)$ notwithstanding its unbound (with respect to $\text{Be} (^1S)$) atomic nature.

The last Be containing species to be presently examined is the homonuclear diatomic $\text{Be}_2 (X^1\Sigma_g^+)$. An extensive bibliographic survey up to 2016 is critically exposed in Ref. [28] and it will not be repeated here.

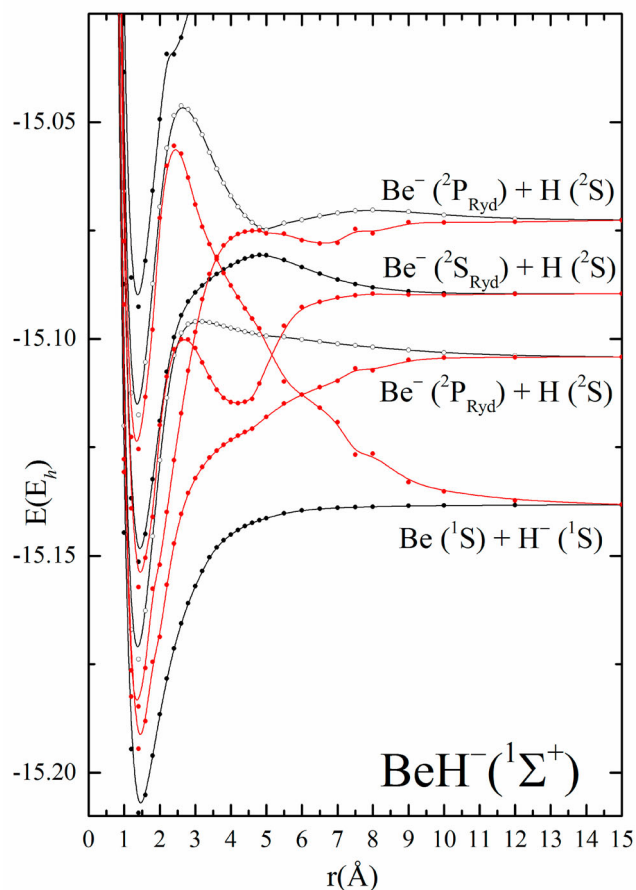


Figure 3. Adiabatic (black curves) and diabatic (red curves) potential energy curves for the BeH^- states of $^1\Sigma^+$ symmetry at the SACASSCF/aug-cc-pVQZ level of theory. Diabatization is treated as a 4×4 problem.

The conclusion reached is that its ground $X^1\Sigma_g^+$ state results from the interaction of two excited 3P states bound together with two nominally sigma bonds.

A recent SCGVVB study [30] on Be_2 concludes that there is a pair of singlet coupled electrons hosted by a set of highly overlapping ($S = 0.83$) ‘inner’ orbitals that constitute a traditional sigma bond and an ‘outer’ pair of singlet coupled electrons in a set of weakly overlapping orbitals ($S = 0.27$) thus having a significant diradical character. It is assumed that the two Be atoms are *in situ* in their ground 1S state and the binding results as a reorganization of the spin couplings of the four valence electrons. Due to an overlap between the ‘inner’ and ‘outer’ orbitals ($S = 0.17$ and 0.34) there is a considerable Pauli repulsion that destabilizes the system by ~ 60 kcal/mol. The same Pauli repulsion is also found as the predominant destabilizing factor in an EDA – NOCV analysis at the BP86/TZ2P computational level [31].

We have constructed both diabatic and adiabatic curves; see Figure 4. Two ground state Be atoms interact

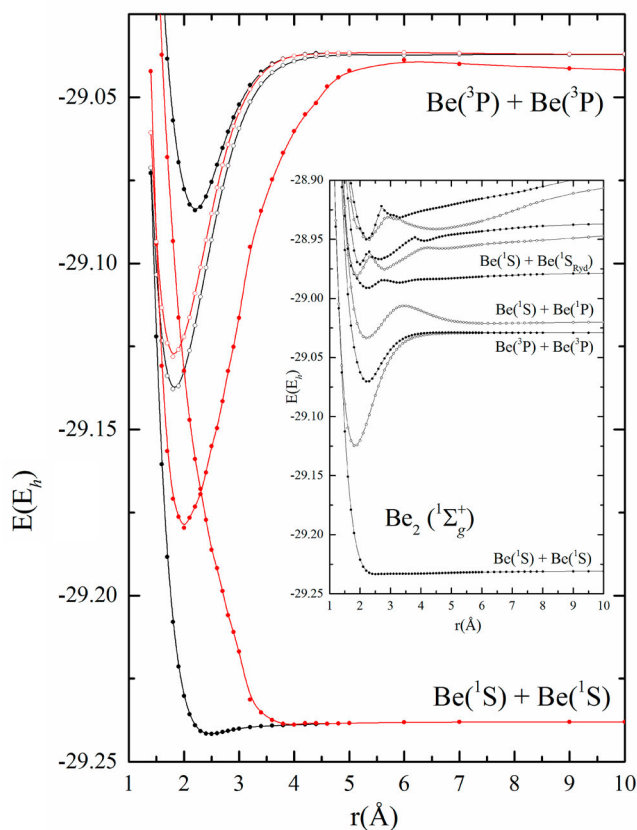


Figure 4. MRCI/aug-cc-pVQZ adiabatic (black curves) and diabatic (red curves) potential energy curves of Be_2 ($1\Sigma_g^+$) dissociating to $\text{Be}(1\text{S}) + \text{Be}(1\text{S})$ and $\text{Be}(3\text{P}) + \text{Be}(3\text{P})$. Several Be_2 states of $1\Sigma_g^+$ symmetry at the SACASSCF level appear in the inset. Diabatization is treated as a 5×5 problem.

purely repulsively due to their closed shell character but two excited 3P ($2s^1 2p^1$) states interfere constructively. Our present findings are in complete harmony with the conclusions reached in Ref. [28], *i.e.* the shallow minimum of the ground beryllium dimer is due to two excited 3P Be atoms.

The O_3 species, a diamagnetic molecule, is believed to feature a *partial* diradical character (30% [32], 24% [33], 20% [34], and 23% [35]) while it is believed to be formed by the association of three $\text{O}(3\text{P})$ atoms. Two singlet coupled electrons are thought to reside primarily on the terminal oxygen atoms [36]. This chemical interpretation was recently challenged. It was proposed instead that ground state O_3 is a genuine closed shell singlet species formed when two excited fragments are held together by a dative bond: $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D}) \rightarrow \cdot\text{O} = \text{O} : \rightarrow \text{O} : (\leftrightarrow : \text{O} \leftarrow : \text{O} = \text{O} :)$ [37]. This conclusion triggered a number of interpretational studies. A QUAOS analysis [38] reported a $\sim 44\%$ of diradical character while the most recent numbers are 19% [39] and 18% [40]. In the latter study the authors concluded that the ground state

originates from $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D})$ as first proposed in Ref. [37]

A recent SCGVB study [41] concluded on its almost complete diradical character based on the low overlap ($S = 0.16$) of the terminal orbitals as found in previous SCGVB calculations [33,34,36]. As it [41] was tailored only for the $\text{O}_2(X^3\Sigma_g^-) + \text{O}(3\text{P})$ interaction it could not consider the mixing with $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D})$ [42,43] and the ensuing dative bond.

In (the inset of) Figure 5 we display the diabatic and adiabatic potential curves of all $1A'$ states resulting from the asymmetric combination $\text{O}_2(X^3\Sigma_g^-) + \text{O}(3\text{P})$ and $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D})$. The repulsive character of the lowest adiabatic potential curve ($\leftarrow \text{O}_2(X^3\Sigma_g^-) + \text{O}(3\text{P})$) up to 1.8 \AA is pretty obvious but beyond this point it plummets due to the interaction with the $3^1A'$ state issued from $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D})$. The diabatic curves show the purely repulsive interaction of O_2

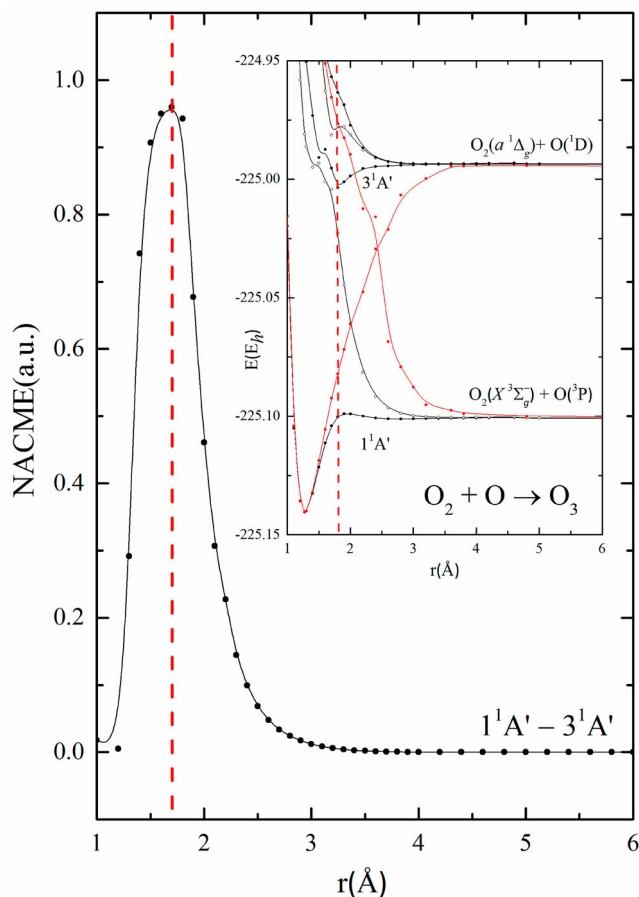


Figure 5. NACMEs of the 1st and 3rd $1A'$ adiabatic states of O_3 along the asymmetric dissociation to their asymptotic products $\text{O}_2(X^3\Sigma_g^-) + \text{O}(3\text{P})$ and $\text{O}_2(a^1\Delta_g) + \text{O}(1\text{D})$, respectively. Adiabatic (black curves) and diabatic (red curves) potential energy curves are shown in the inset. Numerical results at the MRCI/aug-cc-pVQZ computational level. Diabatization is treated as a 5×5 problem.

($X^3\Sigma_g^-$) + O (3P) and the purely attractive interaction of O_2 ($a^1\Delta_g$) + O (1D). Finally, the evolution of the NACMEs is in complete agreement with the form of the adiabatic/diabatic curves. Our present results show that the formation of ground O_3 results from the O_2 ($a^1\Delta_g$) + O (1D) interaction [37,42].

By symmetrically dissociating O_3 to three O atoms we get *mutatis mutandis* an identical picture for the bonding character. The O (3P) + O (3P) + O (3P) interaction is initially repulsive for all states, see Figure 6. For the ground potential profile and for bond distances less than ~ 4 bohr the interaction becomes attractive due to the intervening states correlating to O (3P) + O (3P) + O (1D). Its potential barrier (see inset of Figure 6) is similar to the one displayed in the ground potential profile of the O_2 ($X^3\Sigma_g^-$) + O (3P) interaction (see Figure 5). Both reaction paths, O + O + O and O_2 + O offer a complementary (and identical) analysis of the bond formation. In the O_2 + O case the diabatic origin is the excited O_2 ($a^1\Delta_g$) + O (1D) channel that correlates to O (3P) + O (3P) + O (1D), that is the diabatic origin of the O + O + O combination.

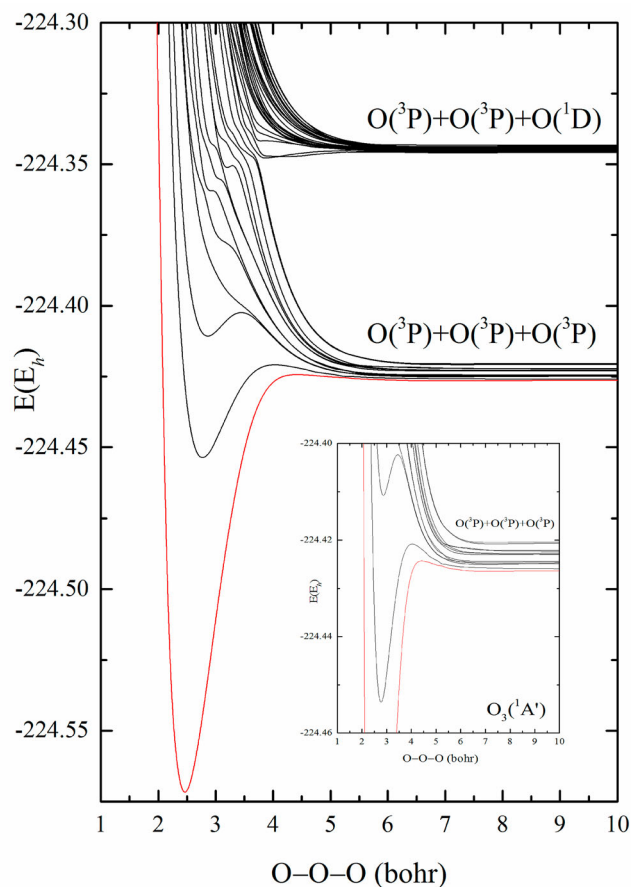


Figure 6. Potential energy profiles of the symmetric dissociation O_3 ($^1A'$) \rightarrow 3O at the SACASSCF/cc - pVQZ computational level.

The last molecular species to be presently examined is the ground state of the atmospherically important CO_3 ; see *e.g.* Ref. [44]. It is considered as an important reaction intermediate for the quenching of electronically excited O (1D) atoms in the atmospheres of Earth and Mars and it also contributes to the anomalous ^{13}O isotope enrichment. It was first postulated in 1962 by Katakis and Taube [45] as an unstable kinetic intermediate in the exchange of oxygen between CO_2 and O (1D) and isolated and characterized by Moll *et al.*, [46] in 1966 and by Weissberger *et al.*, [47] in 1967. Since then it has been the subject of numerous experimental and theoretical studies; see *e.g.* Refs. [48–64], while an historical overview is given in Refs. [60], [61], and [65]. The theoretical studies [48,49,51–55,59–64] were focused primarily on its energetic and geometrical features while some [59,61,63,64] also considered the vibronic effects through a Jahn – Teller and pseudo Jahn – Teller formalism. All computational studies agree on a singlet C_{2v} global minimum with a D_{3h} local minimum at 3.03 kcal/mol (CCSDT/aug - cc - pVQZ) [56], 6.45 kcal/mol (CCSD(TQ)/cc - pVTZ) [61], and 5.5 kcal/mol (CCSD(T)/aug - cc - pVTZ) [63] higher.

In this work we will focus on the bonding features of the (global) C_{2v} minimum by detailing the adiabatic transformations $CO + O_2 \leftarrow CO_3 \rightarrow CO + 2O$. Also of interest is the bonding analysis of the related H_2CO_3 ($(HO)_2CO$) molecular species. As previously found [15] its minimum results from the interaction of $C(OH)_2$ (\tilde{a}^3B_1) + O (3P) or CO ($a^3\Pi$) + $2OH(X^2\Pi)$. By removing the hydrogen atoms of the two OH groups a singlet CO_3 ($\Delta E(\tilde{a}^3E'' \leftarrow \tilde{X}^1A_1) = 25.63$ kcal/mol) species arises with a cyclic C_{2v} structure where the OCO angle drops from 108.63° (H_2CO_3) [15] to 75.25° (CO_3), apparently due to the formation of a loose chemical bond between the two terminal O atoms (but *see below*).

Let us first consider the $CO + O_2$ dissociation path (Figure 7). We adiabatically dissociate the species by retaining the CO and O_2 distances at the CO_3 equilibrium values ($O_{(axial)}CO_2$; $CO_{(axial)} = 1.169$ Å, $CO_{(terminal)} = 1.325$ Å, $O_{(term)}CO_{(term)} = 75.25^\circ$). The (adiabatic) ground exit channel is CO ($X^1\Sigma^+$) + O_2 ($a^1\Delta_g$) that gives rise to an initial repulsive interaction until around 3.5 bohr. Two closed shell singlet CO and O_2 moieties cannot form any bonds and they repel each other but beyond the maximum of their repulsive interaction (~ 3.5 bohr) the triplet CO and O_2 species enter into the chemical scene. The only possible candidate is CO ($a^3\Pi$) while the lowest triplet O_2 candidate is O_2 ($X^3\Sigma_g^-$). There is thus a formation of two C – O bonds between the four electrons of the two triplet coupled fragments ($a^3\Pi + X^3\Sigma_g^-$). The global C_{2v} minimum of CO_3 is fully understood through this formation channel, *i.e.*

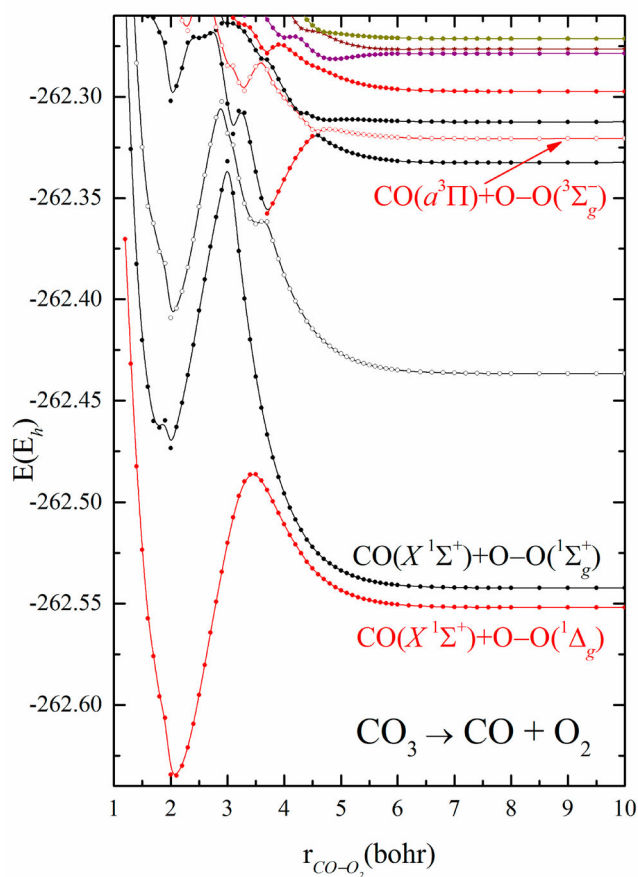


Figure 7. Potential energy profiles of the ground CO_3 state along the $\text{CO} + \text{O}_2$ dissociation path at the SACASSCF/cc – pVQZ computational level. The geometry of the molecular fragments (CO and O_2) is at the equilibrium structure of CO_3 (see text for numerical values). The CO moiety approaches $\text{O} - \text{O}$ vertically along an axis passing from its midpoint.

through the combination of an elongated singly bonded O_2 species with two tripled coupled electrons that are ready to combine with the tripled coupled electrons of an excited CO ($a^3\Pi$) fragment. In agreement with the above picture is the Mulliken atomic population of the $2s^{0.90}$ orbital of carbon at its equilibrium geometry.

The $\text{CO} + 2\text{O}$ path confirms the excited *in situ* character of CO . The ground exit channel finds all of its constituents at their respective ground states, *i.e.*, CO ($X^1\Sigma^+$) and O (^3P) that initially have a repulsive interaction (see Figure 8). At around 4 bohr the ground potential energy curve presents an energy barrier but beyond this point its energy drops due to its interaction with a remote potential curve arising from CO ($a^3\Pi$) + 2 O (^3P). The evolution of the Mulliken populations of the $\text{C } 2s$ orbital is indicative of the participation of the excited $a^3\Pi$ state in the formation process as it plummets from 1.80 (at infinity) to only 0.96 (at equilibrium). Both formation/dissociation paths ($\text{CO} + 2\text{O} \leftarrow \text{CO}_3 \rightarrow \text{CO} + \text{O}_2$) provide an insightful view of its bonding

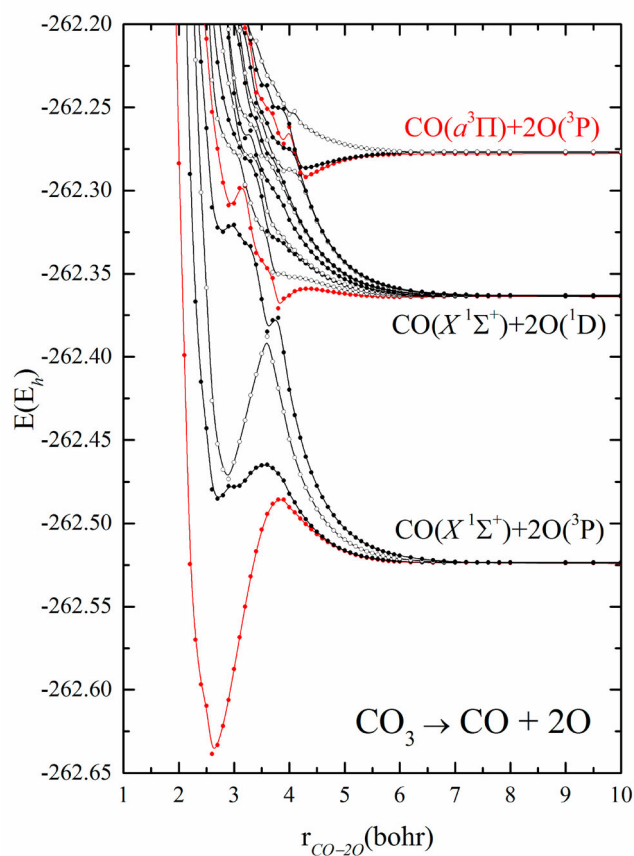


Figure 8. Potential energy profiles of the ground CO_3 state along the $\text{CO} + 2\text{O}$ dissociation path at the SACASSCF/cc – pVQZ computational level.

status with the main characteristic being the $2s^1 2p^3$ C configuration.

4. Conclusions

A discussion on the chemical bonding implies tacitly or explicitly that molecules are made out of atoms bound together in such a way as to decrease their kinetic energy. Ground and excited states of the atomic entities may contribute as well to the formation of the ground molecular states. Within this work we have constructed diabatic curves and NACMEs that show the excited character of the fragments in some simple species like BeH ($X^2\Sigma^+$), BeH^- ($X^1\Sigma^+$), Be_2 ($X^1\Sigma_g^+$), O_3 (\tilde{X}^1A_1). In all Be containing diatomics the Be atom is *in situ* found in its excited ^3P ($2s^1 2p^1$) state while in O_3 both O_2 and O are *in situ* found in their first excited $a^1\Delta_g$ and ^1D states, respectively. Finally, in CO_3 the carbon atom uses all its four valence electrons through an excited $2s^1 2p^3$ carbon electronic configuration.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

- [1] B.T. Sutcliffe, *Adv. Chem. Phys.* **114**, 1 (2000).
- [2] B.T. Sutcliffe and R.G. Wooley, *J. Chem. Phys.* **137**, 22A544 (2012). doi:10.1063/1.4755287
- [3] S.F. Boys, *Rev. Mod. Phys.* **32**, 296 (1960). J.M. Foster, S.F. Boys, *ibid* **32**, 300 (1960). doi:10.1103/RevModPhys.32.296
- [4] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35**, 457 (1963). *ibid*, *J. Chem. Phys.* **43**, S97 (1965). doi:10.1103/RevModPhys.35.457
- [5] J. Pipek, P.G. Mezey and *J. Chem. Phys.* **90**, 4916 (1989).
- [6] K. Ruedenberg, *J. Chem. Phys.* **157**, 024111 (2022). doi:10.1063/5.0094609
- [7] J. Gerratt, *Annu. Rep. Prog. Chem. Sect A* **65**, 3 (1968).
- [8] R.C. Ladner and W.A. Goddard, III, *J. Chem. Phys.* **51**, 1073 (1969). doi:10.1063/1.1672106
- [9] D.L. Cooper, J. Gerratt and M. Raimondi, *Chem. Rev.* **91**, 919 (1991). doi:10.1021/cr00005a014
- [10] T. Thornsteinsson, D.L. Cooper, J. Gerratt, P.B. Karadakov and M. Raimondi, *Theor. Chim. Acta.* **93**, 343 (1996). doi:10.1007/BF01129215
- [11] W. Moffitt, *Proc. Royal Soc. A* **210**, 245 (1951).
- [12] C.A. Nicolaides and Y. Komninos, *Int. J. Quantum Chem.* **67**, 321 (1998). < 321::AID-QUA5 > 3.0.CO;2-X
- [13] Y. Komninos and C.A. Nicolaides, *Int. J. Quantum Chem.* **71**, 25 (1999). < 25::AID-QUA3 > 3.0.CO;2-#
- [14] A. Kalemoss, *Mol. Phys.* **119**, e1804082 (2021). doi:10.1080/00268976.2020.1804082
- [15] A. Kalemoss, *Mol. Phys.* **119**, e1952327 (2021). doi:10.1080/00268976.2021.1952327
- [16] A. Kalemoss, *J. Chem. Phys.* **156**, 214303 (2022). doi:10.1063/5.0088788
- [17] M. Born, *Nachr. Akad. Wiss. Göttingen, II Math–Physik, Kl.* 1951, Nr. 6; M. Born, K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Appendix VIII.
- [18] F.T. Smith, *Phys. Rev.* **179** (111), (1969).
- [19] C.A. Mead and D.G. Truhlar, *J. Chem. Phys.* **77**, 6090 (1982). doi:10.1063/1.443853
- [20] M. Baer, *Beyond Born–Oppenheimer: Electronic Nonadiabatic Coupling Terms and Conical Intesections* (John Wiley & Sons, Hoboken, NJ, 2006).
- [21] MOLPRO is a package of *ab initio* programs written by H.–J.: Werner, P. J. Knowles, G.: Knizia, F. R. Manby, M. Schütz, P. Celani, W. Györffy, D. Kats, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Köppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklaß, D. P. O’Neill, P. Palmieri, D. Peng, K. Pflüger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson and M. Wang. MOLPRO, *version 2012.1, a package of ab initio programs*; University College Cardiff Consultants Limited: Cardiff, U.K., 2008.
- [22] J. Pitarch(Ruiz, J. Sánchez(Marin, A.M. Velasco and I. Martin, *J. Chem. Phys.* **129**, 054310 (2008). doi:10.1063/1.2953584
- [23] D. Yan-Ran, Z. Shu-Dong, H. Sheng-Wei and C. Qi-Yuan, *Chin. Phys. B* **21**, 083104 (2012).
- [24] J. Koput, *J. Chem. Phys.* **135**, 244308 (2011). doi:10.1063/1.3671610
- [25] M. Verdichio, G.L. Bendazzoli, S. Evangelisti and T. Leininger, *J. Phys. Chem. A* **117**, 192 (2013). doi:10.1021/jp310200j
- [26] J. Koput, *J. Chem. Phys.* **139**, 104309 (2013). doi:10.1063/1.4820403
- [27] J.P. Harris, D.R. Manship, W.H. Breckenridge and T.G. Wright, *J. Chem. Phys.* **140**, 084304 (2014). doi:10.1063/1.4865749
- [28] A. Kalemoss, *J. Chem. Phys.* **145**, 214302 (2016). doi:10.1063/1.4967819
- [29] J. Gerratt and M. Raimondi, *Proc. Roy. Soc. London A.* **371**, 525 (1980). doi:10.1098/rspa.1980.0095
- [30] L.T. Xu, T.H. Dunning, Jr., *J. Chem. Phys.* **152**, 214111 (2020). doi:10.1063/5.0010068
- [31] L. Zhao, S. Pan, N. Holzmann, P. Schwerdtfeger and G. Frenking, *Chem. Rev.* **119**, 8781 (2019). doi:10.1021/acs.chemrev.8b00722
- [32] E.F. Hayes and A.K.Q. Siu, *J. Am. Chem. Soc.* **93**, 2090 (1971). doi:10.1021/ja00737a064
- [33] P.J. Hay, T.H. Dunning, Jr. and W.A. Goddard, III, *J. Chem. Phys.* **62**, 3912 (1975). doi:10.1063/1.430306
- [34] P.J. Hay and T.H. Dunning, Jr., *J. Chem. Phys.* **67**, 2290 (1977). doi:10.1063/1.435064
- [35] W.D. Laidig and H.F. Schaefer III, *J. Chem. Phys.* **74**, 3411 (1981). doi:10.1063/1.441494
- [36] W.A. Goddard III, T.H. Dunning, Jr., W.J. Hunt and P.J. Hay, *Acc. Chem. Res.* **6**, 368 (1973). doi:10.1021/ar50071a002
- [37] A. Kalemoss and A. Mavridis, *J. Chem. Phys.* **129**, 054312 (2008). doi:10.1063/1.2960629
- [38] V.–A. Glezakou, S.T. Elbert, S.S. Xantheas and K. Ruedenberg, *J. Phys. Chem. A.* **114**, 8923 (2010). doi:10.1021/jp105025d
- [39] E. Miliordos, K. Ruedenberg and S.S. Xantheas, *Angew. Chem. Int. Ed.* **52**, 5736 (2013). doi:10.1002/anie.201300654
- [40] E. Miliordos and S.S. Xantheas, *J. Am. Chem. Soc.* **136**, 2808 (2014). doi:10.1021/ja410726u
- [41] T.Y. Takeshita, B.A. Lindquist and T.H. Dunning, Jr., *J. Phys. Chem. A.* **119**, 7683 (2015). doi:10.1021/acs.jpca.5b00998
- [42] A. Kalemoss, *J. Phys. Chem. A.* **120**, 169 (2016). doi:10.1021/acs.jpca.5b09431
- [43] The authors of Ref. [41] say: It should, however, be noted that since we only use one set of orbitals and the overall GVB wavefunction must be consistent with the symmetry of the molecule, our calculations would not be able to describe the asymmetric bonding associated with formation of a dative bond at R_e.
- [44] B.C. Ferrari, K. Slavcinska and C.J. Bennett, *Acc. Chem. Res.* **54**, 1067 (2021). doi:10.1021/acs.accounts.0c00731
- [45] D. Katakis and H. Taube, *J. Chem. Phys.* **36**, 416 (1962). doi:10.1063/1.1732521
- [46] N.G. Moll, D.R. Clutter and W.E. Thompson, *J. Chem. Phys.* **45**, 4469 (1966). doi:10.1063/1.1727526

- [47] E. Weissberger, W.H. Breckenridge and H. Taube, *J. Chem. Phys.* **47**, 1764 (1967). doi:10.1063/1.1712161
- [48] B.M. Gimare and T.S. Chou, *J. Chem. Phys.* **49**, 4043 (1968). doi:10.1063/1.1670715
- [49] J.F. Olsen and L. Burnelle, *J. Am. Chem. Soc.* **91**, 7286 (1969). *ibid.*, 92, 3659 (1970). doi:10.1021/ja01054a015
- [50] M.E. Jacox and D.E. Milligan, *J. Chem. Phys.* **54**, 919 (1971). doi:10.1063/1.1675021
- [51] J.A. Pople, U. Seeger, R. Seeger and P.v.R. Schleyer, *J. Comp. Chem.* **1**, 199 (1980). doi:10.1002/jcc.540010215
- [52] S. Canuto and G.H.F. Diercksen, *Chem. Phys.* **120**, 375 (1988). doi:10.1016/0301-0104(88)87223-9
- [53] M.A. Castro, S. Canuto and A.M. Simas, *Chem. Phys. Lett.* **177**, 98 (1991). doi:10.1016/0009-2614(91)90182-9
- [54] R.D.J. Froese and J.D. Goddard, *J. Phys. Chem.* **97**, 7484 (1995). doi:10.1021/j100131a016
- [55] A.S. Averyanov, Y.G. Khait and Y.V. Puzanov, *J. Mol. Struct. (THEOCHEM)*. **459**, 95 (1999). doi:10.1016/S0166-1280(98)00261-9
- [56] E.P. Abreu, M.A. Castro, M.F. Costa and S. Canuto, *J. Mol. Spectry.* **202**, 281 (2000). doi:10.1006/jmsp.2000.8129
- [57] C.J. Bennett, C.S. Jamieson, A.M. Mebel and R.I. Kaiser, *Phys. Chem. Chem. Phys.* **6**, 735 (2004). doi:10.1039/b315626p
- [58] C.S. Jamieson, A.M. Mebel and R.I. Kaiser, *Chem. Phys. Chem.* **7**, 2508 (2006). doi:10.1002/cphc.200600390
- [59] T. Kowalczyk and A.I. Krylov, *J. Phys. Chem. A.* **111**, 8271 (2007). doi:10.1021/jp073627d
- [60] R.I. Kaiser and A.M. Mebel, *Chem. Phys. Lett.* **465**, 1 (2008). doi:10.1016/j.cplett.2008.07.076
- [61] Y. Liu, I.B. Bersuker, W. Zou and J.E. Boggs, *J. Chem. Theor. Comp.* **5**, 2679 (2009). doi:10.1021/ct9002515
- [62] C. Qin and T-Y Soo, *J. Mol. Struct. (THEOCHEM)*. **897**, 32 (2009). doi:10.1016/j.theochem.2008.11.018
- [63] D.A. Hrovat, G.-L Hou, B. Chen, X.-B Wang and W.T. Borden, *Chem. Sci.* **7**, 1142 (2016). doi:10.1039/C5SC03542B
- [64] I. Seidu, P. Goel, X.-G Wang, B. Chen, X.-B Wang and T. Zeng, *Phys. Chem. Chem. Phys.* **21**, 8679 (2019). doi:10.1039/C9CP01352K
- [65] K.V. Krishnamurty, *J. Chem. Ed.* **44**, 594 (1967). doi:10.1021/ed044p594