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How Good Is Koopmans' Approximation? G2(MP2) Study of the Vertical and Adiabatic Ionization Potentials of Some Small Molecules

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Merits and limitations of Koopmans' approximation in estimating the vertical and adiabatic ionization potentials are examined by the G2(MP2) procedure in some small molecules involving first and second row atoms. It is shown that Koopmans' theorem and the corresponding orbital energies provide a very crude approximation to the ionization potentials IPs in a quantitative sense. In fact, vertical and adiabatic potentials are given by an interplay of four and six terms, respectively, which are not simply proportional to the orbital energies and usually do not vary in a predictive way. However, it is possible to find satisfactory linear relations between the orbital energies and both types of the ionization potentials for families of very closely related molecules. On the other hand, the many-body effects are important for a quantitative description of the phenomenon and in interpreting changes in IPs between widely different molecules. A serious discrepancy is found between the G2(MP2), G2, and G3 adiabatic ionization potentials ADIP for a series of molecules NH_nF_{3-n} ($n = 1-3$) and the experimental data. This would suggest a significant contribution of the vibrationally excited states of the ion to the experimental ADIP values, particularly since the predicted vertical ionization potentials are in harmony with the corresponding observed data. The influence of the continuum states, which is not taken into account in the theoretical model, cannot be excluded either. Alternatively, it is possible that the correlation energy is not correctly reproduced in these molecules by the G2(MP2), G2 and G3 computational protocols.

Introduction

A spectacular success of the computational quantum chemistry in the last two decades could be characterized either as a crawling revolution or a fast evolution. Indeed, many observables can be computed nowadays, thanks to efficient numerical algorithms and powerful computers, with accuracy comparable to that obtained by measurements or better than that depending on the type of the experiments. However, theoretical methods and models have one distinctive advantage in addition: they can offer a deep insight into studied phenomena and provide simple and intuitively appealing interpretation of molecular properties.[1] For example, it is possible to analyze nowadays old approximate and qualitative models in a more sound and quantitative way by using modern ab initio methods.[2−4] One of the most famous approximations in the early molecular orbital theory is the so-called Koopmans' theorem stating that the ionization potential IP_n is equal to the negative of the *n*th molecular orbital energy ϵ_n.[5] In fact, this would be an exact solution as calculated within the Hartree−Fock model, if the ionization process were instantaneous and if the correlation energy contribution could be completely neglected. In such a case molecular orbital energies obtained within the frozen orbital and clamped nuclei picture could be directly measured by PES (photoelectron spectroscopy)[5,6] and ESCA (electron spectroscopy for chemical analysis)[7] techniques. The former utilizes UV radiation and expels valence electrons, whereas the latter employs X-rays capable to eject inner core electrons. Not unexpectedly, Koopmans' approximation provides just a crude description of the photoionization process and the one-particle picture of many electron molecules is far from being exact. Nevertheless, Koopmans' theorem has played a paramount role in the development of both PES and ESCA experimental methods providing an invaluable tool in assigning their molecular spectra and offering a simple rationalization of the trends of changes in IPs within families of related molecules. Moreover, Koopmans' theorem has given a simple description of the intramolecular interactions between various fragments and atomic groupings within molecules[8−10] as well as a partial justification of the single electron concept itself within the Hartree−Fock model. A common rationale behind Koopmans' ionization potentials $(IP)_n^{Koop}$ is a tacit assumption that the relaxation of the orbital and nuclei effect is at least approximately canceled out by a difference in the electron correlation energy in the ground state of a molecule (GS) and the radical cation produced by ionization. Is that so? Instead of $(IP)_n^{Koop}$ values, experiments can measure vertical and adiabatic potentials denoted here as $(VIP)_n$ and $(ADIP)_n$, respectively. The former are obtained by keeping nuclei frozen at the GS optimal values during the ionization process thus corresponding to the strongest line of a band, whereas the latter is related to the 0 → 0 transition of a given band and is the true ionization potential,[11] since all degrees of freedom of the electronic and nuclear motion are optimized for both the initial and final states. It is the aim of the present work to examine, by using the G2(MP2) method,[12] various contributions to $(VIP)_1$ and $(ADIP)_1$ values and relate them to Koopmans' ionization potentials $(IP)_n^{Koop}$, i.e., to orbital energies $-\epsilon_1$, since we shall examine the first ionization only corresponding to the highest occupied molecular orbital (HOMO). It should be also pointed out that we consider the ions in their lowest vibrational state. Finally, we shall neglect all relativistic effects, since they are negligible for the outermost electrons of the molecules studied here. The present analysis,

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therefore, will shed light on the performance of the Koopmans' clamped nuclei-frozen electrons approximation for the final radical cation state, thus revealing its usefulness, applicability and limitations.

Theoretical Framework and Computational Procedure

The initial GS geometry is optimized by the MP2(full)/6-31G* model as utilized in the G2(MP2) procedure. The Hartree−Fock total and orbital energies for GS are obtained by the HF/6-311+G(3df,2p)//MP2(full)/6-31G* calculations, since the final correlation energies in the G2(MP2) framework correspond in ultima linea to the 6-311+G(3df,2p) basis set. It is assumed that a considered molecule has n electrons, which is diminished by one upon ionization. Therefore, the radical cation will be denoted by $n - 1$ as a subscript. Hence

$$(\mathrm{IP})_1^{\mathrm{Koop}} = E(\mathrm{HF})_{n-1}^{\mathrm{Koop}} - E(\mathrm{HF})_n = -\epsilon_1 \qquad (1)$$

where $E(\mathrm{HF})_{n-1}^{\mathrm{Koop}}$ is calculated by the clamped nuclei (CN) and frozen orbitals approximation. We note in passing that Koopmans' theorem also assumes that the zero-point vibrational energies (ZPVEs) are equal for a neutral molecule and its ion. Keeping in mind that we examine the first ionization potentials only, index 1 could be dropped. The vertical ionization potentials is given by the HF model as

$$\mathrm{VIP(HF)} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{HF})_n + \Delta(\mathrm{ZPVE})_{n-1,n}^{\mathrm{CN}} \qquad (2)$$

where $\Delta(\mathrm{ZPVE})_{n-1,n}^{\mathrm{CN}} = (\mathrm{ZPVE})_{n-1}^{\mathrm{CN}} - (\mathrm{ZPVE})_n$. Here, the contribution of the ZPVEs is explicitly included, which is necessary if a comparison with experiment is desired. Formula 2 implies that orbitals are relaxed, but the nuclei are kept fixed. Further, explicit account of the electron correlation yields

$$\mathrm{VIP[G2(MP2)]} = E[\mathrm{G2(MP2)}]_{n-1}^{\mathrm{CN}} - E[\mathrm{G2(MP2)}]_n \qquad (3)$$

Since the correlation energy E(corr) is defined as a positive quantity for the sake of convenience, we obtain

$$E[\mathrm{G2(MP2)}]_{n-1}^{\mathrm{CN}} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{corr})_{n-1}^{\mathrm{CN}} + (\mathrm{ZPVE})_{n-1}^{\mathrm{CN}} \qquad (4)$$

and

$$E[\mathrm{G2(MP2)}]_n = E(\mathrm{HF})_n - E(\mathrm{corr})_n + (\mathrm{ZPVE})_n \qquad (5)$$

which by insertion to eq 3 yields

$$\mathrm{VIP[G2(MP2)]} = \mathrm{VIP(HF)} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} \qquad (6)$$

where $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} = E(\mathrm{corr})_n - E(\mathrm{corr})_{n-1}^{\mathrm{CN}}$. Formula 6 is a consequence of the fact that the ZPVEs in the G2(MP2) procedure are calculated at the Hartree−Fock level, which in turn are absorbed in the VIP(HF) term. The correlation energy for n electrons is larger than for $n - 1$ electrons as a rule. Hence $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ is expected to be positive, implying that it leads to higher VIP[G2(MP2)] values. It is clear that the HF vertical ionization potentials VIP(HF) can be expressed by Koopmans' $-\epsilon_1$ orbital energy and the orbital relaxation of the radical cation with nuclei kept fixed at the GS equilibrium positions:

$$\mathrm{VIP(HF)} = -\epsilon_1 + E_{\mathrm{r}}(\mathrm{orb})_{n-1}^{\mathrm{CN}} + \Delta(\mathrm{ZPVE})_{n-1,n}^{\mathrm{CN}} \qquad (7)$$

where

$$E_{\mathrm{r}}(\mathrm{orb})_{n-1}^{\mathrm{CN}} = E(\mathrm{HF})_{n-1}^{\mathrm{CN}} - E(\mathrm{HF})_n + \epsilon_1 \qquad (8)$$

Thus, the final formula reads

$$\mathrm{VIP[G2(MP2)]} = -\epsilon_1 + E_{\mathrm{r}}(\mathrm{orb})_{n-1}^{\mathrm{CN}} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} + \Delta(\mathrm{ZPVE})_{n-1,n}^{\mathrm{CN}} \qquad (9)$$

In other words, the vertical ionization potential is given by Koopmans' clamped nuclei and frozen orbitals value $-\epsilon_1$ corrected by the orbital relaxation in the $n - 1$ state by keeping the nuclei fixed and by adding up a difference between the correlation energy in GS and radical cation $n - 1$, again by holding nuclei tight at the GS equilibrium positions. The last term gives a difference between the ZPVEs of the radical cation and the initial neutral molecule. It would be of interest to see whether these non-Koopmans' terms $E_{\mathrm{r}}(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ and $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ cancel out to some extent and whether a change in the ZPVEs caused by ionization has any significant influence on the vertical ionization potentials.

Let us focus on the adiabatic ionization potential (ADIP) now:

$$\mathrm{ADIP[G2(MP2)]} = E[\mathrm{G2(MP2)}]_{n-1} - E[\mathrm{G2(MP2)}]_n \qquad (10)$$

or alternatively,

$$\mathrm{ADIP[G2(MP2)]} = [E(\mathrm{HF})_{n-1} - E(\mathrm{HF})_n] + [E(\mathrm{corr})_n - E(\mathrm{corr})_{n-1}] + \Delta(\mathrm{ZPVE})_{n-1,n} \qquad (11)$$

Here all quantities are fully relaxed and optimized and $\Delta(\mathrm{ZPVE})_{n-1,n} = (\mathrm{ZPVE})_{n-1} - (\mathrm{ZPVE})_n$. However, it is useful to imagine the adiabatic ionization as a two-step process. The first step corresponds to the vertical ionization, where the $n - 1$ state is described within the CN approximation. Subsequently, the structural parameters of the $n - 1$ radical cation are relaxed, thus completing the adiabatic ionization. Let us define the corresponding changes in the relaxation and electron correlation energies as

$$E_{\mathrm{r}}(\mathrm{nucl})_{n-1} = E(\mathrm{HF})_{n-1} - E(\mathrm{HF})_{n-1}^{\mathrm{CN}} \qquad (12)$$

and

$$\Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}} = E(\mathrm{corr})_{n-1}^{\mathrm{CN}} - E(\mathrm{corr})_{n-1} \qquad (13)$$

where $E_{\mathrm{r}}(\mathrm{nucl})_{n-1}$ is also defined as a positive quantity. Here, the superscript RN denotes relaxed nuclei. Then one obtains

$$\mathrm{ADIP[G2(MP2)]} = \mathrm{VIP[G2(MP2)]} + E_{\mathrm{r}}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}} + \Delta(\mathrm{ZPVE})_{n-1,n-1}^{\mathrm{RN}} \qquad (14)$$

where $\Delta(\mathrm{ZPVE})_{n-1,n-1}^{\mathrm{RN}} = (\mathrm{ZPVE})_{n-1} - (\mathrm{ZPVE})_{n-1}^{\mathrm{CN}}$. Consequently, the adiabatic IP is obtained by the vertical ionization potential by taking into account correction due to the radical cation relaxation by switching off the clamped nuclei approximation and a change in the correlation energy due to the optimization of the radical cation geometry. In some more detail ADIP[G2(MP2)] takes a form

$$\mathrm{ADIP[G2(MP2)]} = -\epsilon_1 + E_{\mathrm{r}}(\mathrm{orb})_{n-1}^{\mathrm{CN}} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} + E_{\mathrm{r}}(\mathrm{nucl})_{n-1} + \Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}} + \Delta(\mathrm{ZPVE})_{n-1,n-1}^{\mathrm{RN}} \qquad (15)$$

Finally, it should be mentioned that the neutral molecules are treated by the restricted HF and G2(MP2) models, whereas the

TABLE 1: Various Contributions Determining VIPs and ADIPs and Comparison with Experimental Data (kcal/mol)

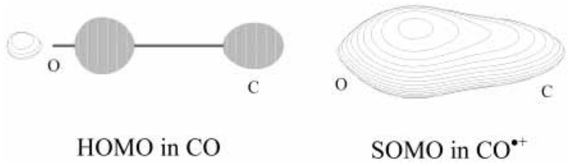
molecule	$-\epsilon_1$	$E_r(\mathrm{orb})^{CN}_{n-1}$	$\Delta E(\mathrm{corr})^{CN}_{n,n-1}$	$\Delta(\mathrm{ZPVE})^{CN}_{n-1,n}$	VIP[G2(MP2)]^a	$E_r(\mathrm{nucl})_{n-1}$	$\Delta E(\mathrm{corr})^{RN}_{n-1,n-1}$	$\Delta(\mathrm{ZPVE})^{RN}_{n-1,n-1}$	ADIP[G2(MP2)]^a
CO	350.0	−47.7	21.7	−0.8	323.2 [323.1]	−5.4	4.7	0.8	323.3 [323.2 ± 0.1]
CS	289.7	−61.3	36.0	−0.3	264.1	0.3	−1.1	0.1	263.4 [261.3 ± 0.2]
HF	407.6	−78.0	44.6	−0.4	373.8 [371.7 ± 0.9]	0.1	−1.5	−1.2	371.0 [369.7 ± 0.9]
LiH	187.7	−27.8	24.1	−0.1	183.9	−5.6	2.4	−1.2	179.5 [182.2]
LiF	298.8	−67.6	47.9	−0.1	279.0	−14.8	−0.3	−1.1	262.8 [260.6]
HCl	299.6	−33.6	27.6	−0.2	293.4	−0.1	−0.2	−0.2	292.9 [293.9 ± 0.2]
N_2	377.5	−18.6	−1.0	−0.6	357.3 [359.3]	2.8	−2.2	0.4	358.3 [359.3 ± 0.2]
NH_3	270.2	−52.9	36.5	0.5	253.3 [250.2]	−18.2	0.5	−0.6	235.0 [232.3 ± 0.5]
NH_2Me	246.8	−52.3	33.5	−1.0	227.0 [222.5]	−17.7	0.8	−0.3	209.8 [205.2 ± 2.3]
$NHMe_2$	233.0	−54.4	32.7	−0.7	210.6 [206.9]	−18.2	1.4	−0.5	193.3 [190.0 ± 1.8]
NMe_3	224.2	−56.5	32.8	−0.3	200.2 [197.4]	−19.4	2.3	−0.6	182.5 [181.0 ± 1.2]
NH_2F	297.7	−50.6	21.7	−1.6	267.2 [268.0]	−36.2	9.7	0.3	241.0 [249.7]
NHF_2	324.9	−48.6	11.8	−2.0	286.1 [285.5]	−45.0	17.9	1.4	260.4 [265.9 ± 1.8]
NF_3	355.6	−49.1	12.1	−1.9	316.7 [317.1]	−46.3	17.9	2.5	290.8 [298.4 ± 0.2]
PH_3	241.6	−26.3	27.0	−0.4	241.9 [244.2]	−17.9	2.5	0.4	226.9 [227.6 ± 0.1]
PH_2Me	226.1	−29.2	26.9	−0.5	223.3 [223.7]	−18.0	2.3	0.3	207.9 [210.3 ± 1.6]
$PHMe_2$	215.0	−31.7	26.9	−0.3	209.9 [209.9]	−19.2	2.6	0.1	193.4 [195.3]
PMe_3	206.6	−33.9	27.3	0.1	200.1 [198.3]	−20.4	3.4	−0.2	182.9 [186.8 ± 2.3]
PH_2F	249.8	−25.4	22.0	−0.6	245.8	−20.5	7.0	0.9	231.4
PHF_2	262.0	−24.9	17.8	−0.9	254.0 [253.7]	−22.5	8.0	1.1	240.6 [242.1 ± 2.3]
PF_3	296.9	−28.0	16.4	−0.5	284.8 [283.2]	−31.6	9.2	1.1	263.5 [262.4 ± 2.3]
H_2O	320.0	−67.1	41.4	−0.9	293.4 [291.0]	0.0	−1.3	−0.7	291.4 [291.0 ± 0.1]
MeOH	283.7	−60.1	34.7	−2.1	256.2 [253.7]	−0.5	−3.0	0.2	252.9 [250.0 ± 0.2]
Me_2O	267.1	−62.8	33.5	−1.5	236.3 [232.9]	−4.8	0.4	−0.1	231.8 [231.2 ± 0.6]
HOF	345.3	−75.0	27.7	−1.3	296.7	−5.6	1.1	0.3	292.5 [293.1 ± 0.2]
F_2O	370.0	−85.8	23.6	−1.1	306.7 [305.8]	−7.8	2.1	0.7	301.7 [302.3]
H_2S	241.7	−29.3	27.6	−0.2	239.8 [240.5]	0.0	−0.1	0.1	239.8 [241.1 ± 0.3]
MeSH	224.3	−32.7	27.3	−0.5	218.4 [217.7]	−0.7	−0.1	0.1	217.7 [217.7 ± 0.1]
Me_2S	210.8	−35.5	27.2	−0.5	202.0 [200.6]	−1.6	0.2	0.0	200.6 [200.4 ± 0.5]
HSF	249.7	−28.8	19.7	−0.4	240.2	−7.8	3.8	0.6	236.8
F_2S	255.3	−28.5	12.6	−0.4	239.2	−15.8	8.1	0.8	232.3 [232.4]
OH^-	66.3	−72.9	49.7	−0.1	43.0	−0.1	0.0	0.4	43.3
MeO^-	66.4	−66.1	43.1	−1.6	60.5	−9.2	2.6	2.7	37.9
SH^-	59.0	−34.3	28.4	0.0	53.1	−0.1	0.1	0.2	53.3
MeS^-	52.0	−36.6	28.0	−0.7	42.7	−1.4	0.4	1.5	43.2

[a] Available experimental data are placed within square parentheses and are taken from ref 16.

radical cations are considered by the corresponding unrestricted methods, that is to say, by the UHF and UG2(MP2) procedures.

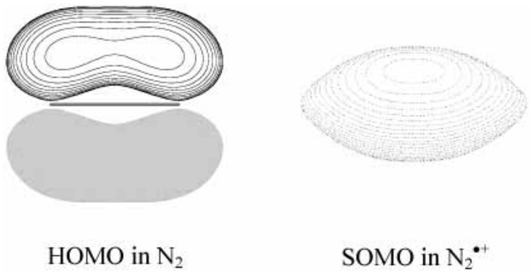
Results and Discussion

Results are summarized in Table 1. Let us commence discussion with diatomics. It is obvious that $E_r(\mathrm{orb})^{CN}_{n-1}$ and $\Delta E(\mathrm{corr})^{CN}_{n,n-1}$ have opposite signs, but they do not cancel out. On the contrary, their sum is always negative since $E_r(\mathrm{orb})^{CN}_{n-1}$ prevails. It is noteworthy that the lowest $E_r(\mathrm{orb})^{CN}_{n-1}$ values are found in two diatomics involving fluorine atom (HF and LiF), thus indicating that it might be a consequence of its electronegativity (vide infra). On the other hand, $E_r(\mathrm{nucl})_{n-1}$ and $\Delta E(\mathrm{corr})^{RN}_{n-1,n-1}$ contributions to ADIP[G2(MP2)] are relatively small and of the opposite sign as a rule. As a result, they do cancel out to a very large extent in some cases, thus making the adiabatic potential practically equal to the vertical one. LiF provides one of the notable exceptions, where $E_r(\mathrm{nucl})_{n-1}$ assumes a very low value −14.8 kcal/mol. The reason behind



HOMO in CO SOMO in CO$^{\bullet+}$

Figure 1. HOMO in CO and the singly occupied MO in the σ-radical CO$^{\bullet+}$.



HOMO in N_2 SOMO in $N_2^{\bullet+}$

Figure 2. HOMO in N_2 and the singly occupied SOMO in $N_2^{\bullet+}$.

this is that the Li−F radical cation bond distance is very long ($d(\mathrm{Li{-}F})^{\bullet+} = 2.339$ Å), meaning that a withdrawal of the clamped nuclei condition leads to a large energy gain. It is worthwhile to point out that the HOMO in CO is a linear combination of the σ lone pair local orbitals placed at carbon and oxygen atoms. The HOMO in CO and SOMO (single occupied molecular orbital) in CO$^{\bullet+}$ are depicted in Figure 1, which shows that CO$^{\bullet+}$ is a σ radical. In contrast, the HOMO and SOMO have different symmetries in N_2 (see later). Agreement with available experimental data is good. G2(MP2) results usually deviate 2−3 kcal/mol from measured values in diatomics. Generally speaking, the average absolute error for VIP[G2(MP2)] and ADIP[G2(MP2)] are 1.6 and 2.2 kcal/mol, respectively, if all studied molecules are taken into account. Discrepancies encountered in some fluorine derivatives will be commented upon later. This degree of accuracy lends credence to conclusions derived from computations. It should be pointed out as a final general observation that $E(\mathrm{corr})_{n-1}^{\mathrm{CN}}$ and $E(\mathrm{corr})_{n-1}$ terms are quite close in most cases, implying that the correlation energy is not very sensitive to a small change in geometric parameters. Let us consider the case of the N_2 molecule. The HOMO is a doubly degenerate π-MO level, whereas the SOMO corresponds to a σ-combination of the lone pair orbitals (Figure 2). Consequently, Koopmans' theorem predicts a wrong symmetry for the resulting positive ion. Perusal of the data presented in Table 1 shows that the N_2 molecule owes its high vertical and adiabatic potentials to rather low lying HOMO level(s). Another peculiarity of the nitrogen molecule is a fact that the orbital relaxation energy $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ is small (in the absolute sense) compared to other diatomics. Moreover, $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}} = -1$ kcal/mol, implying that the correlation energies of the neutral molecule and its cation are practically equal in the CN approximation. The nitrogen molecule is unique in this respect, taking into account systems studied in the present work (Table 1). Next, we shall focus on NH_3, H_2O, PH_3, and H_2S and their CH_3 and F derivatives. The methyl group is a representative of an electron donor substituent, whereas F is the paradigmatic electron acceptor. Consider CH_3 derivatives first. It appears that $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ is lower in oxygen compounds than in nitrogen ones. Similarly, the orbital relaxation of the cation at frozen nuclei is lower in sulfur compared to phosphorus molecules. Obviously, $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ is lower (i.e., it is larger in the absolute value) for more electronegative atoms, which is not unreasonable. Another important observation is that $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ predominates over $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ for the first row atoms N and O, implying that VIP[G2(MP2)] is substantially lower than IP$^{\mathrm{Koop}}$ since $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ is a negative quantity. In contrast, these two terms practically cancel out for the second row elements, e.g., in H_2S and PH_3. Successive methylation of these compounds increases in its absolute value $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ but lowers its true negative values, presumably because of the increasing number of the first row atoms, i.e., carbons. Consequently, a sum $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}} + \Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ becomes negative, albeit moderately. Whereas interplay between $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ and $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ depends on the row of the participating atoms, $E_r(\mathrm{nucl})_{n-1}$ is dependent on the column. Consider the following two families of molecules NH_nMe_{3-n} and PH_nMe_{3-n} ($n = 1-3$). The reorganization energy $E_r(\mathrm{nucl})_{n-1}$ due to relaxation of the nuclei assumes values between −18 and −20 kcal/mol. The corresponding change in the correlation energy $\Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}}$ is small in the PH_nMe_{3-n} series (∼3 kcal/mol) being almost negligible in the NH_nMe_{3-n} series, trimethylamine being an exception. As a consequence, ADIP[G2(MP2)] is by 15−18 kcal/mol smaller than VIP[G2(MP2)]. A completely different situation takes place in OH_nMe_{2-n} and SH_nMe_{2-n} ($n = 1, 2$) molecules, where both $E_r(\mathrm{nucl})_{n-1}$ and $\Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}}$ are rather small, meaning that the vertical and adiabatic potentials are very close. This conclusion is corroborated both by the computations and by the experiments. Let us consider now the effect of fluorination. While the methylation has led to a decrease in $-\epsilon_1$ with concomitant lowering of VIP and ADIP values, the contrary takes place upon fluorination. It appears that the HOMOs and their orbital energies ϵ_1, belonging to the lone pair of the central atom N or P, are increasingly stabilized with each additional fluorine atom. Both vertical and adiabatic potentials are enlarged too. This holds for both amino and phosphine series. It turns out also that a substitution of the CH_3 group with the F atom does not change the $E_r(\mathrm{orb})_{n-1}^{\mathrm{CN}}$ term appreciably. In contrast, $\Delta E(\mathrm{corr})_{n,n-1}^{\mathrm{CN}}$ becomes significantly smaller for fluorinated amines, whereas at the same time $E_r(\mathrm{nucl})_{n-1}$ and $\Delta E(\mathrm{corr})_{n-1,n-1}^{\mathrm{RN}}$ assume substantially lower and higher values, respectively. This occurs in fluorinated phosphines too, but to the much less pronounced extent. Apparently, there are no easy generalizations, which would allow a simple prediction of the ionization potentials. Instead, one has to accept the fact that VIPs and ADIPs are results of an interplay of 4 and 6 terms, respectively, which do not change always in a predictable fashion. Having said that, it is gratifying that one can extract from the data given in Table 1 correlations of VIPs and ADIPs with ϵ_1 orbital energies for substituted amines and phosphines, which are quite acceptable at least at the semiquantitative level. Let's consider first NH_nX_{3-n} ($n = 1-3$) series, where X=CH_3, F. The least-squares fit method yields

$$\mathrm{VIP[G2(MP2)]}_N = 0.8478\epsilon_1 + 15.12\ \mathrm{kcal/mol} \quad (16)$$

with $R^2 = 0.987$ and the average absolute error $\Delta_{\mathrm{av}} = 3.4$ kcal/mol. Analogously,

$$\mathrm{ADIP[G2(MP2)]}_N = 0.7664\epsilon_1 + 16.65\ \mathrm{kcal/mol} \quad (17)$$

with $R^2 = 0.974$ and $\Delta_{\mathrm{av}} = 4.8$ kcal/mol. Obviously, the quality of the correlation for the vertical potential is relatively good, whereas the ADIPs are less satisfactorily described by Koopmans' theorem, as one could intuitively expect. One cannot resist saying, however, that fairly high Δ_{av} values illustrate an obvious

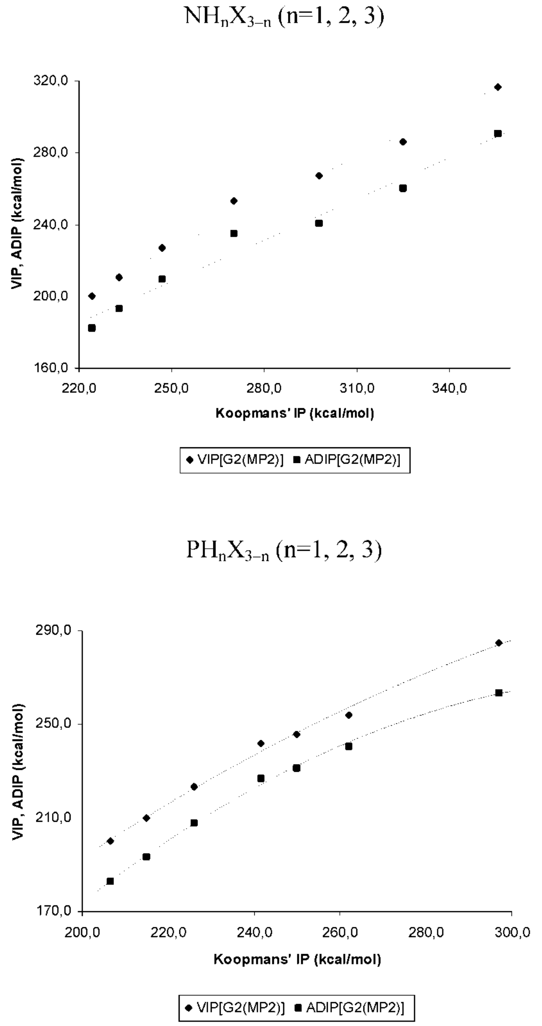


Figure 3. Relations between the vertical and adiabatic ionization potentials against negative of the orbital energies $-\epsilon_1$ in substituted ammonia and phosphine ($X = CH_3$, F).

fact that much is still left to be desired. It should be mentioned that a quadratic fitting function did not offer any improvement over the linear relations (16) and (17). Inspection of the straight lines on Figure 3 shows that NH_3 lies somewhat off in both correlation. Its exclusion improves the correlation for ADIPs, as evidenced by increased $R^2 = 0.991$. In contrast to amines, quadratic fitting of Koopmans' IPs to vertical and adiabatic potentials for phosphines PH_nX_{3-n} ($n = 1-3$), where again X = CH_3, F, did improve the quality of the correlations:

$$\mathrm{VIP[G2(MP2)]}_P = -0.0028(\epsilon_1)^2 + 2.3312\epsilon_1 - 161.4 \text{ kcal/mol} \quad (18)$$

The corresponding R^2 and Δ_{av} are 0.995 and 1.4 kcal/mol, respectively. The adiabatic ionization potentials are given by

$$\mathrm{ADIP[G2(MP2)]}_P = -0.0053(\epsilon_1)^2 + 3.5613\epsilon_1 - 326.0 \text{ kcal/mol} \quad (19)$$

where $R^2 = 0.998$ and $\Delta_{av} = 1.3$ kcal/mol. Somewhat counterintuitively the adiabatic potentials are slightly better described by the orbital energies $-\epsilon_1$ than the vertical ones. A poorer performance of the linear correlations for the adiabatic ionization potentials ADIPs is not surprising: the latter are determined by five different terms (viz. formula 15) in addition to the orbital energy $-\epsilon_1$. One could epitomize this analysis by saying that Koopmans' theorem provides reasonably good results for intimately related molecules. However, many-body terms become important in accurate (i.e., quantitative) description of the ionization process and in discussing changes in the IPs between widely different molecules. Let us consider, for example, the vertical ionization potentials between N_2 and NMe_3. It is useful to introduce a tetrad $\Delta(\mathrm{VIP[G2(MP2)]}) = (-\Delta\epsilon_1, \Delta E_r(\mathrm{orb})^{\mathrm{CN}}_{n-1}, \Delta\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}, \Delta\Delta(\mathrm{ZPVE})^{\mathrm{CN}}_{n-1,n})$, where changes in the four terms of eq 9 are given as components. Obviously, $\Delta(\mathrm{VIP[G2(MP2)]})$ is given by a sum of components within the tetrad. The difference $\mathrm{VIP[G2(MP2)]}(N_2) - \mathrm{VIP[G2(MP2)]}(NMe_3)$ is then provided by $\Delta(\mathrm{VIP[G2(MP2)]}) = (153.3, 37.9, -33.8, -0.3)$, which gives a final value of 157.1 kcal/mol. It is worth mentioning that $\mathrm{VIP[HF]}(N_2) - \mathrm{VIP[HF]}(NMe_3) = 191.0$ kcal/mol, which illustrates importance of the correlation energy effect. Similarly, $\mathrm{VIP[G2(MP2)]}(N_2) - \mathrm{VIP[G2(MP2)]}(NF_3)$ is given by $\Delta(\mathrm{VIP[G2(MP2)]}) = (21.9, 30.5, -13.1, 1.3)$, yielding a difference of 40.6 kcal/mol. Whereas in the former case the influence of the orbital energy ϵ_1 was overwhelming, in the latter the Koopmans' one-electron energy and the many-body effects have comparable influence on $\Delta(\mathrm{VIP[G2(MP2)]})$. This type of analysis can be extended to the adiabatic potentials too. The bottom line is that the many-electron effects are far from being negligible.

Finally, it should be mentioned that for fluorinated amines theory and experiment are in sharp disagreement as far as the adiabatic potentials ADIP[G2(MP2)] are concerned. In an attempt to settle the problem, we carried out G2 and G3[12] calculations of the ADIPs in the series NH_3, NH_2F, NHF_2, and NF_3. The corresponding values are 235.0 [233.8], 241.4 [240.6], 260.9 [260.3], and 291.4 [291.2] in kcal/mol, respectively, where G3 results are given within the squared parentheses. Hence, more refined methods corroborate results of the G2(MP2) computational protocol. Since the measured data are always higher than the theoretical results, this finding indicates an appreciable contribution of the higher vibrational states in the ions. The influence of the continuum states[13,14] cannot be excluded either, but they would affect VIPs too, which was not found here at least not to a considerable extent (Table 1).

The third group of compounds studied here are anions OH^-, MeO^-, SH^-, and MeS^-. They are known as Lewis' bases.[15] The most striking feature is that both VIPs and ADIPs are rather small. The reason behind this is a low $-\epsilon_1$ value, which is subsequently lowered by other terms in formula 15. However, it is important to emphasize that anions behave somewhat differently than neutrals. For example, $E_r(\mathrm{orb})^{\mathrm{CN}}_{n-1}$ is larger in its absolute value than $\Delta E(\mathrm{corr})^{\mathrm{CN}}_{n,n-1}$, as expected, but the negative orbital energies $-\epsilon_1$ are very small, leading to low VIP and ADIP values. Finally, a survey of the $\Delta(\mathrm{ZPVE})^{\mathrm{CN}}_{n-1,n}$ and $\Delta(\mathrm{ZPVE})^{\mathrm{RN}}_{n-1,n-1}$ terms (Table 1) shows that they are small varying between -2.0 and $+2.5$ kcal/mol. Obviously, they have to be taken explicitly into account if accurate ionization potentials are desired. It is noteworthy that $\Delta(\mathrm{ZPVE})^{\mathrm{CN}}_{n-1,n}$ and $\Delta(\mathrm{ZPVE})^{\mathrm{RN}}_{n-1,n-1}$ have different signs in most cases, meaning that their sum entering formula for the ADIP[G2(MP2)] is rather small.

To conclude, Koopmans' theorem does not offer an accurate description of either vertical or adiabatic ionization potentials. Hence, its remarkable success in rationalizing molecular spectra can be traced to fairly good correlations with the experimental data for families of very closely related molecules. It is also fair to say that Koopmans' theorem does reproduce a broad trend of changes in the ionization potentials for widely different molecules, but only in a qualitative sense.

Concluding Remarks

Ab initio G2(MP2) analysis of the vertical and adiabatic ionization potentials shows that the gross effect is given by the orbital energy contribution $-\epsilon_1$ of a single electron, as stated by Koopmans' theorem. However, Koopmans' approximation is inadequate in many ways. It does not include the relativistic effects, which are important for inner electrons of the heavier atoms. Further, Koopmans' theorem sometimes predicts the wrong symmetry of the resulting positive ion. A classical example is given by the N_2 molecule, where according to Koopmans' approximation one should expect the $^2\Pi_u$ state of the cation, whereas experiment shows that the latter is in the $^2\Sigma_g^+$ state.[17]

The quantitative description of the first vertical and adiabatic ionization potentials of molecules involving atoms of the first and second period of the system of elements requires inclusion of several important many-electron corrections. On the other hand it is found that the influence of the ZPV energies is very small. It is important to emphasize that the correlation and relaxation energies do not change in a simple and predictable manner, unless a series of intimately related molecules is considered. In that case satisfactory linear or quadratic relations can be found between VIP and ADIP values on one side and orbital ϵ_1 energies on the other, as, e.g., in families of molecules NH_nX_{3-n} ($X = CH_3$, F) or PH_nX_{3-n} ($X = CH_3$, F) where $n = 1-3$. We found a sharp disagreement between ADIPs of fluorinated amines calculated by G2(MP2), G2, and G3 computational procedures and experimental data. A source of these discrepancies is probably given by the higher excited vibrational states of the ions. A moderate influence of the molecular continuum states cannot be excluded either. Alternatively, it is possible that the electron correlation energy is not correctly reproduced in these molecules by the G2(MP2), G2 and G3 computational protocols.

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