

Electronic Interaction in Heterosubstituted Acetones studied by Means of Ultraviolet Photoelectron and Electron Transmission Spectroscopy

Paulo R. Olivato and Sandra A. Guerrero

Instituto de Química, Universidade de São Paulo, São Paulo, Brasil

Alberto Modelli

Istituto Chimico 'G. Ciamician' dell'Università di Bologna, Via Selmi 2, Bologna, Italy

Gaetano Granozzi

Istituto di Chimica Generale ed Inorganica, Università di Padova, Via Loredan 4, Padova, Italy

Derek Jones and Giuseppe Distefano*

Istituto dei composti del carbonio contenenti eteroatomi e loro applicazioni del CNR, Via Tolara di sotto 89, 40064 Ozzano-Emilia, Bologna, Italy

The He^I and He^{II} photoelectron and the electron transmission spectra of some heterosubstituted acetones CH₃COCH₂X [X = F, Cl, Br, I, SC₂H₅, OCH₃, N(CH₃)₂, and C₂H₅] have been recorded. They have been interpreted with the help of *ab initio* computations using the pseudopotential method of Barthelat *et al.* The energy trend of the MOs mainly localised at the carbonyl group (π_{CO} , π_{CO}^* , and n_O) is discussed in terms of the various electronic interactions with the group orbitals of the X substituent. Finally, the n_O - π_{CO}^* energy gap is related to the variation of the energy of the $\pi_{CO}^* \leftarrow n_O$ u.v. transition.

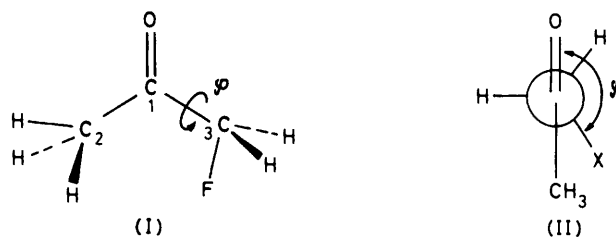
A bathochromic shift and a hyperchromic effect of the $\pi^* \leftarrow n$ band in the u.v. absorption spectra of α -substituted ketones compared with the corresponding unsubstituted or alkyl-substituted derivatives have been reported previously. These effects along with a shift in the carbonyl stretching frequency were interpreted¹⁻³ as deriving from hyperconjugative interaction between the π_{CO}^* and σ_{C-X}^* orbitals. This hyperconjugative interaction, which stabilises the π_{CO}^* orbital, was assumed to reduce the n - π^* energy gap and therefore the energy of the transition. This explanation had been previously applied to the red shift induced in the cyclohexanone $\pi^* \leftarrow n$ transition by axial halogen substituents.⁴ Available u.v. photoelectron data^{1,5} indicate, however, that the energy of the carbonyl lone pair n_O changes with the substituent, and this can also influence the energy of the $\pi^* \leftarrow n$ transition.



- (1) X = F
- (2) X = Cl
- (3) X = Br
- (4) X = I
- (5) X = SEt
- (6) X = OMe
- (7) X = NMe₂
- (8) X = Et

For a fuller understanding of the electronic interaction between a carbonyl group and different α -substituents, a series of mono-substituted acetones (1)–(7) and (8) were analysed here by means of u.v. photoelectron and electron transmission⁶ spectroscopies (u.p.s. and e.t.s.). With the help of theoretical calculations, such experimental data give information on the energy and localisation properties of the filled and empty valence MOs. Our interest centred on the MOs mainly localised on the CO group (π_{CO} , π_{CO}^* , n_O)[†] and on X (X_{1p} , σ_{C-X} , and σ_{C-X}^*)[‡].

[†] π_{CO} and π_{CO}^* indicate the filled and empty π -MOs mainly localised at the carbonyl group. n_O is the carbonyl lone pair MO; X_{1p} is the lone pair orbital(s) mainly localised at the heteroatom of the substituent; σ_{C-X} and σ_{C-X}^* are the filled and empty MOs mainly localised at the C-X bond.



From microwave analyses fluoroacetone is known⁷ to have all the heavy atoms in a plane, with oxygen and fluorine in the *trans*-position [(I) ϕ 180°: ϕ is assumed to be 0° for the *cis*-rotamer]. Dipole moment measurements indicate⁸ that chloro- and bromo-acetone assume predominantly the *gauche*-conformation (II) (ϕ 130° and 120°, respectively⁸). I.r. data on these and other derivatives³ confirmed the predominance of the *gauche*-conformation.[‡]

Experimental

The He^I and He^{II} u.p. spectra were recorded by means of a Perkin-Elmer PS18 photoelectron spectrometer equipped with a Helectros He^{II} lamp. The spectra were calibrated with noble gas lines. The error in the quoted ionization energy (IE) values is ≤ 0.05 eV.

The e.t. spectra were recorded by means of a spectrometer in the format devised by Sanche and Schulz⁶ described elsewhere.⁹ Unfortunately, decomposition did not allow the e.t. spectra of derivatives (3) and (4) to be recorded. The error in the quoted attachment energy (AE) values [which are close to the negative of the vertical electron affinity (EA) values] is ± 0.05 or ± 0.1 eV depending on the number of decimal digits reported.

Calculations

Ab initio LCAO-MO-SCF calculations on the derivatives (1)–(3) and (8) were carried out using the non-empirical pseudo-

[‡] A value of ϕ 0° for (8) has been also reported (C. Romers and J. G. Creutzberg, *Recl. Trav. Chim. Pays-Bas*, 1956, 75, 33).

potential method of Barthelat *et al.*¹⁰ This method offers the advantage of a consistent level of accuracy along the series of halogen derivatives (1)–(3). All calculations were carried out using the PSHONDO program.¹¹ Double-zeta quality basis sets¹² were used and these were optimised, using a modified version¹³ of the ATOM program.¹⁴

Hyperconjugation as well as the other mesomeric interactions are conformation dependent and the gas-phase conformation of the heteroacetones, except that of (1), are unknown. Here they were assumed to be the same as the solution conformations.^{7,8} In any case, for a clearer understanding of the electronic interaction between the X and the CO groups, the computations were carried out for three different values of ϕ (180, 135, and 90°) for the halogen derivatives (1)–(3) and with ϕ 135° for (8).

The energy and localisation properties of the MOs of interest resulted to be only slightly dependent on ϕ for the fluorine derivative (1). Similarly, only small variations were encountered for (2) and (3) on changing ϕ from 180 to 135°, except for the $\pi_{\text{CO}}-\pi_{\text{C-X}}$ and $\pi_{\text{CO}}^*-\pi_{\text{C-X}}^*$ interactions which will be discussed below in some detail.

As expected, larger hyperconjugative interactions were noted at ϕ 90°, especially for (2). However, the total energy of this rotamer of (2) is much higher than that of the other conformers indicating a low probability for its existence in the gas phase.

Unfortunately, convergence difficulties were encountered with the methoxy derivative. For this reason, no computations were attempted for the sulphur and nitrogen derivatives.

Results and Discussions

Assignment of Spectra.—The e.t. spectra are shown in Figure 1 and the He^I and He^{II} u.v. photoelectron spectra of chloro-, bromo-, and iodo-acetone, as examples, are presented in Figure 2. The experimental AE and IE values are presented in diagrammatic form in Figures 3 and 4 and the computed orbital energies (F, ϕ 180°; Cl, Br, and Et, ϕ 135°) in Figure 5.

The clear analogies of the trends in Figures 3 and 5 allow an easy assignment of the various spectral features to the corresponding MOs of the halogenoacetones. In particular, the bands corresponding to electron capture into, or ejection from, the π_{CO}^* , π_{CO} , n_{O} , and X_{1p} orbitals can be easily recognized in all cases. The assignment of the ionization bands is confirmed by the analysis of the intensity variations of corresponding bands on changing the ionizing radiation. On going from He^I to He^{II} spectra, the bands corresponding to MOs rich in N, O, and F p -atomic orbitals increase in intensity, those related to MOs of mainly C_{2p} character are almost unaffected, and the intensity of those rich in S, Cl, Br, and I p -orbitals decreases.^{15–19}

For S, O, and N derivatives, however, the assignment of the band associated with the π_{CO} MO is less certain than for the halogen derivatives due to the lack of computations and to the contribution to the same energy region of ionization from MOs mainly localised at the alkyl groups.

We now discuss in some detail the MOs mainly localized at the CO group, namely n_{O} , π_{CO} , and π_{CO}^* , and, lastly, we will correlate the energy of the u.v. $\pi^* \leftarrow n$ transition with the energy of the MOs involved. The discussion will be mainly centred on the halogen derivatives for which theoretical computations are available.

The Carbonyl Lone Pair Orbital, n_{O} .—The n_{O} orbital is mainly localised at the oxygen atom (45–55%) and at the three carbon atoms. The relative energy of the n_{O} and X_{1p} group orbitals influences their energy and composition in the molecule. In fact, the n_{O} MO is localised to a sizeable extent at the X atom (*ca.* 20%) when X = Cl and Br, whereas the

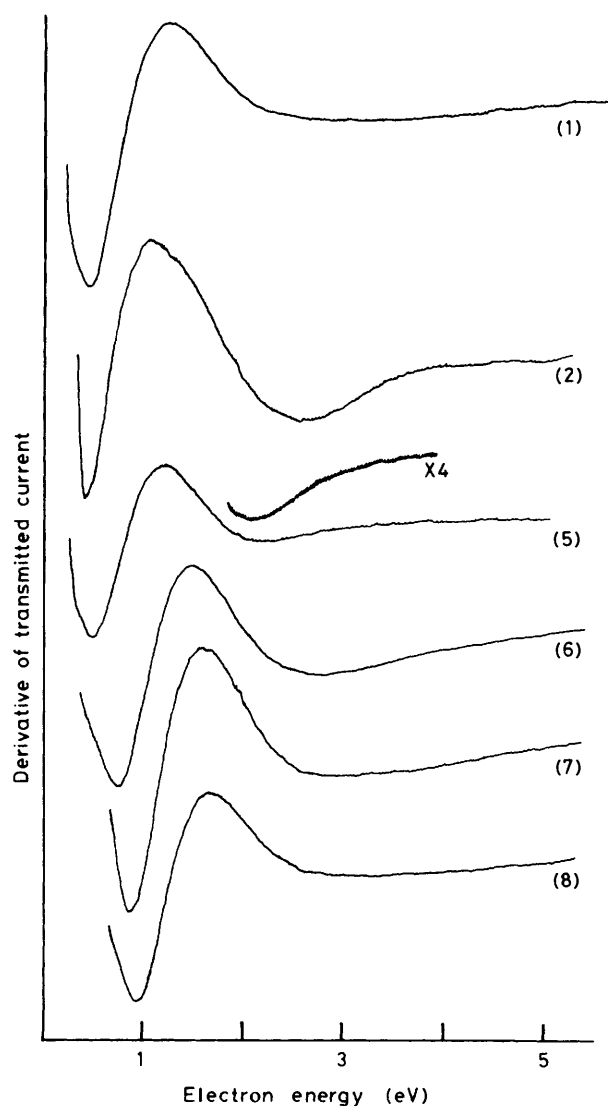


Figure 1. Electron transmission spectra of monosubstituted acetones $\text{CH}_3\text{COCH}_2\text{X}$ [X = F, Cl, SC_2H_5 , OCH_3 , $\text{N}(\text{CH}_3)_2$, and C_2H_5]

contribution to n_{O} from X is nearly absent when X = F and C_2H_5 .

$X_{1p}-n_{\text{O}}$ orbital mixing will certainly also occur in the S, O, and N derivatives. This mixing could explain the higher IE value related to the n_{O} MO in the S derivative compared with the oxygen analogue, despite the smaller heteroatom electronegativity. In fact, due to the inverted relative energy position, in the former the n_{O} orbital is stabilised by interaction with the X_{1p} orbital, while in the latter it is destabilised.

The $X_{1p}-n_{\text{O}}$ orbital interaction occurs through bonds when $\phi = 180^\circ$ and through bonds and space²⁰ for smaller ϕ values. The energy and localisation properties of the n_{O} orbital do not change significantly on changing ϕ from 180 to 135°.

The largest $X_{1p}-n_{\text{O}}$ interaction probably occurs in the iodine derivative where the energy gap is very small. Their mixing is clearly indicated by the relative intensity variations of the first two bands in the He^{II} spectrum. In fact, a larger increase and a larger decrease would be expected for the first and second band, respectively, if they were pure n_{O} and X_{1p} in character (see Figure 2).

It is also to be noted that the trend of the computed n_{O} IE values is equal to the experimental one, except for X = Br

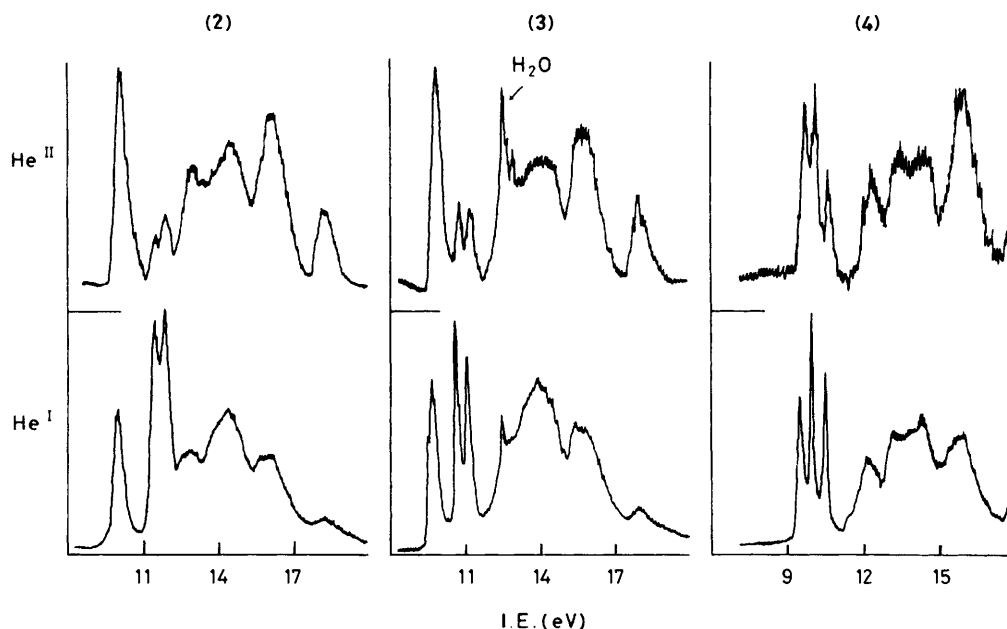


Figure 2. He^I (lower) and He^{II} spectra of heteroacetones CH₃COCH₂X (X = Cl, Br, and I). The sharp peak at 12.62 eV in the spectra of bromoacetone is due to the presence of water

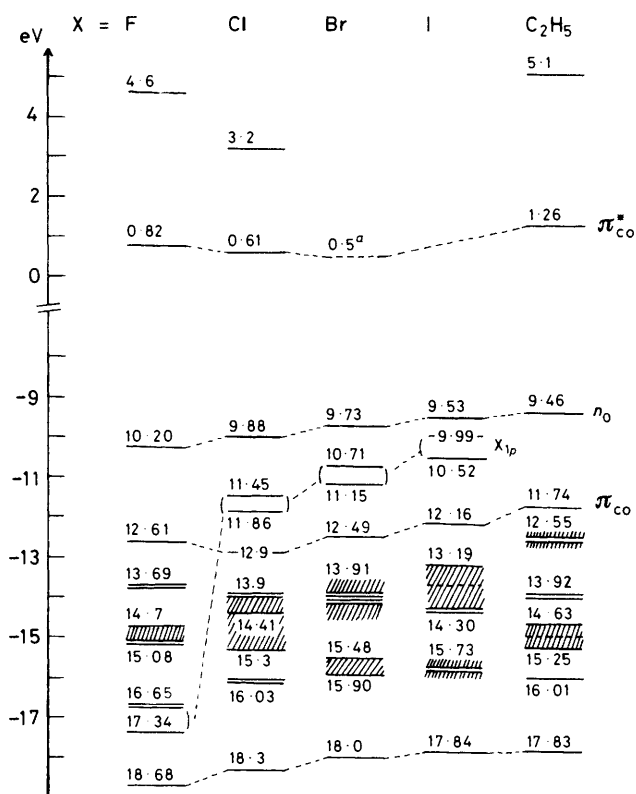


Figure 3. Experimental (u.p.s. and e.t.s.) energy level diagrams for the heteroacetones CH₃COCH₂X (X = F, Cl, Br, I, and C₂H₅). ^aEstimated value, see text.

whose computed value is too high. This is because the X_{1p}-n_O ordering is reversed in the calculation, resulting in a net stabilisation of the n_O orbital.

The Carbonyl π_{CO} Orbital.—The π_{CO} MO is mainly localised at C(1) (ca. 20%) and at oxygen (ca. 50%) with smaller

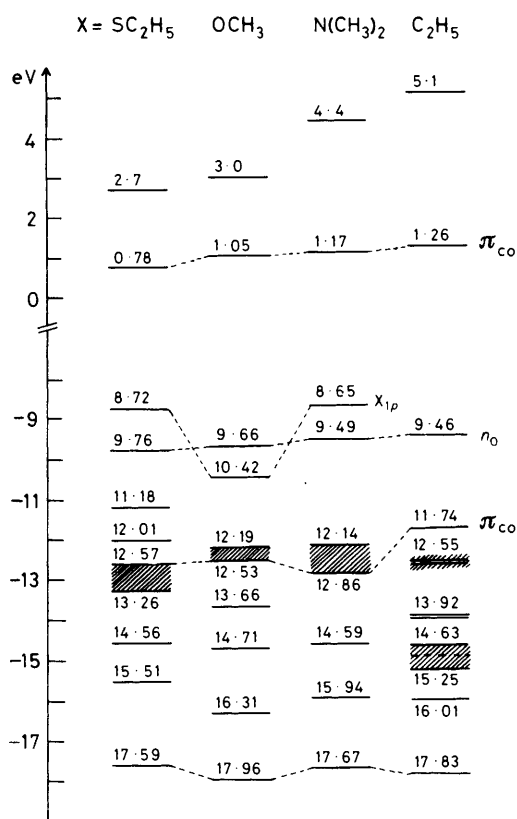


Figure 4. Experimental (u.p.s. and e.t.s.) energy level diagrams for the heteroacetones CH₃COCH₂X [X = SC₂H₅, OCH₃, N(CH₃)₂, and C₂H₅]

contributions from the CH₃ and CH₂ group orbitals. Mixing with the X_{1p} and σ_{C-X} orbitals also occurs. The former decreases and the latter increases on decreasing ϕ from 180 to 90°. Mixing of the π_{CO} and X atom orbitals is greatest in the

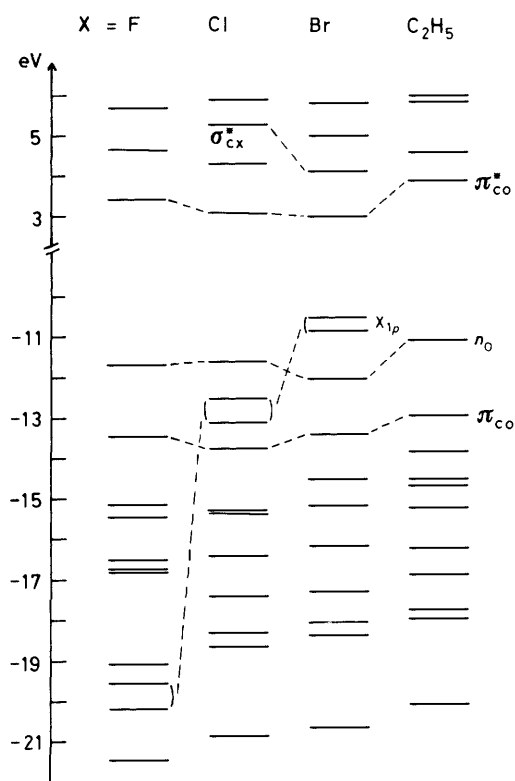


Figure 5. Computer energy level diagrams for the heteroacetones $\text{CH}_3\text{COCH}_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and } \text{C}_2\text{H}_5$) in the *gauche*-form ($\phi 135^\circ$) and for fluoroacetone ($\phi 180^\circ$)

bromine derivative. In fact, the greatest contribution from the AOs of X to the π_{CO} MO increases steadily from 4% ($\text{X} = \text{F}$; $\phi 180^\circ$) to 10% ($\text{X} = \text{Cl}$; $\phi 135^\circ$) to 15% ($\text{X} = \text{Br}$; $\phi 135^\circ$). The destabilising hyperconjugative interaction with the $\sigma_{\text{C-X}}$ orbital increases in the same way.

The energy of the π_{CO} MO depends also on the relative energy of the X_{1p} orbitals and on the electronegativity of X. In particular, the mixing of the π_{CO} MO with the low lying fluorine π -lone pair orbital results in an IE value of 12.61 eV which is smaller than that of the chlorine compound (12.9 eV) despite the higher electronegativity of fluorine and the destabilising hyperconjugative interaction present in $\text{CH}_3\text{COCH}_2\text{Cl}$.

The Carbonyl π_{CO} Orbital.—The energy of the π_{CO} orbital of the substituted acetones is smaller than that of methyl n-propyl ketone, the reference compound. This stabilisation cannot simply be ascribed to the electron-withdrawing inductive effect of the heteroatom, because the π_{CO} orbital is more stable in the chlorine and ethylthio derivatives than in the fluorine and methoxy derivatives, respectively.

The electron affinity of unsaturated systems generally increases when a second row element (Cl, S, or Si) is substituted for a first row element (F, O, or C, respectively),^{9,21-25} This observed stabilisation has been related to several factors, e.g. involvement in bonding of the heteroatom empty *d* orbitals, geometric variations, and hyperconjugative interactions. Considering that in the present case the substituent is bonded to the π system through a CH_2 group, the $\pi_{\text{CO}}^*-\sigma_{\text{C-X}}$ interaction should be particularly important. By analogy with the hyperconjugative interaction between the corresponding filled orbitals considered above, the participation of the bromine AOs to the lowest unoccupied MO (π_{CO}^*) (28%) is larger than that of chlorine (10%). The corresponding participation of the fluorine

MOs is negligibly small. Consequently, the calculated energy of the π_{CO}^* MO decreases on increasing the atomic number of the halogen.

Unfortunately, sample decomposition during introduction did not allow us to obtain the e.t. spectra of the heavy halogen derivatives. However, it is possible to obtain the AE related to the π_{CO}^* MO of the bromo derivative (0.5 eV, see Figure 3) by linear extrapolation of the experimental against the computed values of derivatives (1), (2), and (8).

An analogous increase in the hyperconjugative interaction with increasing atomic number of the heteroatom could explain the higher (0.3 eV) electron affinity of the SEt derivative compared with the OMe one. However, the same effect could be produced by $\text{S}_{3d}-\pi_{\text{CO}}^*$ interaction.

In line with the observed trend in other chlorine²³ and sulphur^{21,22} derivatives, in the e.t. spectra of (2) and (5) a second low-energy resonance is present which can be associated with electron capture into $\sigma_{\text{C-X}}^*$ MOs.

Correlation between the n_{O} and π_{CO}^* Energy and the Energy of the $\pi_{\text{CO}}^* \leftarrow n_{\text{O}}$ Transition.—Equation (1) correlates the energy of a singlet u.v. transition with the energy of the MOs involved in the transition where *J* and *K* are the Coulomb and exchange integrals.²⁶

$$E = \epsilon_{\pi^*} - \epsilon_n - J + 2K \quad (1)$$

With the assumption that for corresponding transitions in a series of closely related molecules the *J* and *K* integrals do not change significantly, the variations of the transition energies (ΔE_i) are given by equation (2). Thus, the energy of the u.v. transition can be simply related to the energy difference between the involved MOs, or, assuming the validity of Koopmans' theorem, to the difference between the relevant experimental electron affinity and ionization energy values.

$$\Delta E_i = \Delta(\epsilon_{\pi^*} - \epsilon_n) \quad (2)$$

On this basis, it was proposed¹⁻⁴ that the red shift observed for the $\pi^* \leftarrow n$ transition in the α -thio- and α -halogen-substituted ketones with respect to the parent unsubstituted or alkyl substituted derivatives was mainly due to the hyperconjugative interaction between the π_{CO}^* and $\sigma_{\text{C-X}}^*$ MOs resulting in a stabilisation of the former orbital.

The present IE and EA data, however, indicate that the $\pi_{\text{CO}}^*-n_{\text{O}}$ energy gaps in compounds (5) and (8) are nearly equal (10.54 and 10.65 eV, respectively), both orbitals in the sulphur derivative being similarly stabilised by the interplay of the electronic interactions. Therefore, variations of the *J* and *K* integrals or solvent effects should contribute to the 0.33 eV decrease of the $\pi_{\text{CO}}^* \leftarrow n_{\text{O}}$ transition energy observed in the sulphur derivative.³

In the halogen-substituted series $\text{CH}_3\text{COCH}_2\text{X}$, the transition energy decreases steadily by 0.3 eV (F, 280; Cl, 291; Br, 300 nm).³ The increasing importance of the hyperconjugative interaction with the $\sigma_{\text{C-X}}^*$ orbital in determining the energy of the π_{CO}^* MO in the chlorine and bromine derivatives has been shown above. However, in this case also, the red shift observed on going from fluoro- to bromo-acetone does not seem to be simply related to the stabilisation of the LUMO. In fact, along the series, the $n_{\text{O}}-\pi_{\text{CO}}^*$ energy gap decreases by 0.8 eV (see Figure 3).

Acknowledgements

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