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Geometry Changes on Negative Ion Formation

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Summary Changes in bond length which accompany negative ion formation in small molecules are discussed in terms of a simple model.

It was demonstrated recently how a simple model, based on electronegativities, could account for geometry changes on ionisation in heteronuclear molecules.[1] The formation of negative ions also involves a change in geometry, although until the advent of laser photoelectron spectrometry (LPS)[2] there has been little reliable experimental evidence on negative ion bond lengths. A Franck–Condon factor analysis is used to estimate the magnitude, but not the direction, of the change in geometry produced by the LPS experiment. The purpose of the present Communication is to show that rules analogous to those given for positive ion geometries[1] may be applied to obtain the direction of the geometry change on negative ion formation.

In principle, the electron introduced to form the negative ion may occupy either a bonding (b), nonbonding (nb), or antibonding (ab) orbital with respect to a particular bond (polarised A^+B^-). The sign of the subsequent change in r_{AB} follows from simple electrostatic considerations in the case of nonbonding orbitals (Types I and II) or from changes in bonding when b_{AB} or ab_{AB} are occupied (Types III and IV).

Type I $A^+B^- + e^-(nb_A) \rightarrow A^\circ B^-$ Δr = positive

Type II $A^+B^- + e^-(nb_B) \rightarrow A^+B^{2-}$ Δr = negative

Type III $A{-}B + e^-(b_{AB}) \rightarrow (A{-}B)^-$ Δr = negative

Type IV $A{-}B + e^-(ab_{AB}) \rightarrow (A{-}B)^-$ Δr = positive

Table. Experimental and theoretical geometry changes on negative ion formation

	Orbital type occupied	Negative ion formation process	Δr_{AB}/Å	Reference[a]
Gas phase				
NO	ab_{NO}	IV	+0·05	3
CO_2	ab_{CO}	IV	+0·12	4
Crystal structures:				
CN	nb_C	I	+0·003	5, 6
OH	nb_O	II	−0·18	5
NO_2	nb_N/ab_{NO}	I/IV	+0·04	7, 5
ClO_2	ab_{ClO}	IV	+0·10	7, 5
Theoretical calculations:				
BH_3	nb_B	I	+0·13	8
CH_3	nb_C	II	−0·04	9
OH	nb_O	II	−0·03	9
SH	nb_S	II	−0·03	9
CN	nb_C	I	+0·05	10
CF	nb_C/ab_{CF}	I/IV	+0·20	11
NF	nb_N/ab_{NF}	I/IV	+0·09	12
NaO[b]	nb_{Na}	I	+0·11	13
NaO	nb_O	II	−0·03	13
PO	nb_P/ab_{PO}	I/IV	+0·02	14
N_2O	ab_{NN}	IV	+0·08	15
N_2O	ab_{NO}	IV	+0·14	15

[a] When two references are given, the first refers to the neutral and the second to the negative ion. [b] nb_{Na} refers to NaO^-, $^3\Pi$, nb_O to $^1\Sigma$.

Several reliable experimental[3–7] and theoretical[8–15] results are listed in the Table. Although it is not justifiable to compare directly geometries obtained from the gas phase with crystal structures, four examples are given in the Table which show that the predictions of the model are not contradicted. The results for the CN–CN^- pair are confirmed by the high quality calculations of Pacansky and Liu,[10] and the negative sign for Δr_{OH} in the OH–OH^- pair has been obtained by many calculations.[9] For the theoretical results given in the Table, either an analogous and extensive basis set was used for both systems, or (for Me, OH, and SH) the average value of a set of (independent) negative ion calculations is compared with the experimental geometry of the neutral molecule. All these *ab-initio* results substantiate the simple model described by the set of rules given above for Δr_{AB}.

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