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Original Investigations

Some Theoretical Aspects of Vibrational Fine Structure Accompanying Core Ionizations in N_2 and CO

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Ab initio calculations have been carried out on CO and N_2 and the relevant core hole states with different basis sets to investigate differences in geometries and force constants. From these calculations vibrational band profiles of the core level ESCA spectra for these molecules have been interpreted, obviating the need to rely on data pertaining to the equivalent core species. The agreement with experimental profiles is excellent. The O_{1s} level of CO which has not been subjected to detailed theoretical analysis previously, is predicted to show substantial vibrational structure in excellent agreement with recently acquired experimental data. The effect of temperature on the band profiles has also been considered. Theoretically derived core binding and relaxation energies of these systems have been investigated both as a function of basis set, and of internuclear distance. Density difference contours have been computed and give a straightforward pictorial representation of the substantial electron reorganizations accompanying core ionizations. Small basis sets with valence exponents appropriate to the equivalent core species when used in hole state calculations describe bond lengths, force constants, core binding energies and relaxation energies with an accuracy comparable to that appropriate to the corresponding extended basis set calculations.

Key words: N_2 – CO – Core ionization

1. Introduction

The advent of high resolution ESCA instrumentation incorporating efficient X-ray monochromatization has recently revealed for the first time vibrational effects accompanying core ionizations [1–3]. The most detailed experimental and theoretical studies to date relate to CH_4, N_2 and CO [1–3]. The experimental data pertaining to photoionization of the C_{1s} and N_{1s} core levels in these systems have been interpreted semi-quantitatively in terms of computed Franck-Condon factors with vibrational frequencies and bond lengths being derived from equivalent cores species [1–3]. The good overall agreement between calculated and experimental profiles for these systems suggests that the analysis presented to date is basically sound [1–3]. However previous theoretical studies indicate that although in general the bond lengths and force constants for equivalent core and hole state species are closely similar, nonetheless small but significant differences are apparent [4]. A detailed theoretical investigation therefore of the potential energy surfaces for core ionized species in the particular case of N_2 and CO would appear to be particularly apposite at this time. For these uncomplicated systems the possibility exists of a detailed non-empirical study incorporating an investigation of the basis set dependence of the computed parameters. We report here the results of such an investigation in which we have studied *inter alia*, equilibrium bond lengths and force constants for neutral molecules, hole states and absolute binding energies and electronic reorganizations accompanying core ionizations.

The theoretically computed force constants, vibrational energy separations, and equilibrium bond lengths have then been used to calculate Franck-Condon factors and hence band profiles for the core ionized states of CO and N_2.

In a previous paper [4] we have discussed in detail the dependence of (electronic) relaxation energies for core ionized species on the detailed electronic structure of the molecular system. In continuation of such investigations the relaxation accompanying core ionizations for N_2 and CO has been studied by means of density difference contours which lead to a straightforward physical interpretation of the computed changes in bond lengths for the core ionized species.

2. Computational Details

Calculations have been carried out within the Hartree Fock formalism since a large body of literature already exists to suggest that changes in correlation energy are relatively unimportant in discussing equilibrium bond lengths, force constants, and absolute binding energies for core levels of first row elements [4–7]. Non-empirical LCAO MO SCF calculations have therefore been carried out on potential energy surfaces for ground and hole states and equivalent core species. The calculations have been performed using the ATMOL system of programs [8] implemented on an IBM 370/195. The basis sets employed were as follows:

(1) STO 4.31G [9] and HF 4.31G [10] using best atom exponents [11];
(2) double zeta Slater using best atom exponents [12];
(3) extended Slater basis set which we refer to as triple zeta Slater, using best atom exponents [13];
(4) for hole states STO 4.31G and HF 4.31G, with valence exponents appropriate to the equivalent core species and these we refer to as "optimized" basis sets [4, 11].

The motivation for employing the basis sets described in (4) was supplied by our previously recorded observations that [4, 14, 15] the partial optimization of exponents yields absolute binding energies in excellent agreement with experiment at a relatively small computational expense and as a viable alternative to carrying out extended basis set calculations. We have also briefly investigated comparable "optimized" double zeta Slater basis sets and our observations are discussed in a later section.

3. Results and Discussion

3.1. Bond Length Optimizations and Force Constants

As a preliminary to studying the equilibrium geometries and force constants for the core ionized species, an investigation has been made of both the neutral

Table 1. Geometries of N_2, CO, NO^+, CF^+ corresponding to minimum energies (in atomic units) and respective force constants (in millidynes per angstrom)

Basis	ReN_2	ReCO	$ReNO^+$	$ReCF^+$	ΔRe (N_2–NO^+)	ΔRe (CO–NO^+)	ΔRe (CO–CF^+)	KeN_2	KeCO	$KeNO^+$	$KeCF^+$
HF 4.31G	2.080	2.164	2.024	2.264	0.056	0.139	−0.100	—	—	—	—
STO 4.31G	2.124	2.167	2.050	2.220	0.074	0.116	−0.053	28.10	22.10	—	—
Double Zeta	2.082	2.155	2.058	2.306	0.024	0.098	−0.151	—	—	—	—
Triple Zeta	2.047	2.123	1.983	2.218	0.064	0.140	−0.095	25.10	19.46	28.90	12.71
Experimental	2.074[a]	2.132[a]	2.007[a]	—	0.067	0.125	—	22.96[b]	19.00[b]	24.85[c]	—

[a] Sutton,L.E.: Tables of interatomic distances Supplement, Special Publication No. 18. London: Chemical Society, Burlington House 1965.
[b] Herzberg,G.: Spectra of diatomic molecules, 2nd Ed. New York: Van Nostrand 1950.
[c] Kharitonov,Yu.Ya.: Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk 1953 (1962).

Table 2. Geometries of $\overset{*}{N}_2$, $\overset{*}{C}O$ and $C\overset{*}{O}$ corresponding to minimum energies (in atomic units) and respective force constants (in millidynes per angstrom)

Basis	$Re\overset{*}{N}_2$	ΔRe (N_2–$\overset{*}{N}_2$)	$Re\overset{*}{C}O$	ΔRe (CO–$\overset{*}{C}O$)	$ReC\overset{*}{O}$	ΔRe (CO–$C\overset{*}{O}$)	$Ke\overset{*}{N}_2$	$Ke\overset{*}{C}O$	$Ke\overset{*}{C}\overset{*}{O}$
HF 4.31G	2.094	−0.014	2.104	0.060	2.316	−0.151	—	—	—
HF 4.31G (Opt.)	2.038	0.043	2.040	0.125	2.281	−0.116	—	—	—
STO 4.31G	2.121	0.004	2.107	0.060	2.266	−0.099	—	—	—
STO 4.31G (Opt.)	2.060	0.064	2.059	0.108	2.237	−0.070	30.70	30.70	15.05
Double Zeta	2.058	0.024	2.052	0.104	2.324	−0.168	—	—	—
Triple Zeta	2.002	0.045	2.010	0.113	2.230	−0.107	29.60	28.90	13.11

molecules and equivalent cores species. The procedure adopted in each case was to start from the experimental geometries and compute parabolas from a grid corresponding to an extension or compression of 0.1 a.u. A process of successive refinement was then carried out in which the minima were taken as starting points and the intervals were decreased to final values of 0.01 a.u. which corresponded to a minimum of ten calculations. In the particular case of CF^+ the starting geometry appropriate to the minimized CO* oxygen hole state (discussed in the next section) was employed. The calculated bond lengths as a function of basis set are compared with the experimental values in Table 1. Considering firstly CO and N_2 it is clear that even at the STO 4.31G level the equilibrium bond lengths are quite accurately reproduced (within ~3%). This is also true for NO^+ and by extrapolation for CF^+.

Having computed energy minima for these systems it is clearly of some importance to establish that the shape of the potential energy curve in the vicinity of the minima is also adequately described. In each case the potential surface in the region corresponding to extension or compression by ~0.15 a.u. was examined and fitted to a parabola. This involved the computation of a few extra points such that a minimum of 15 points were available for each curve. For this purpose only the STO 4.31G and triple zeta basis sets were investigated.

The derived force constants are also given in Table 1. As might be expected the small basis set tends to overestimate the experimental force constants somewhat (by ~25%) whilst the triple zeta basis set gives a more accurate representation. It is clear however that even the small basis set adequately reflects the steeper potential surface of N_2 with respect to CO (ratio of force constants calculated 1.27, experimental 1.21).

Having established that to varying degrees of accuracy as a function of basis set the bond lengths and force constants for these ground state systems may be treated within the Hartree Fock formalism, we may now proceed to investigate the hole states for N_2 and CO also as a function of basis set. The analysis for the N_{1s}, C_{1s} and O_{1s} localized hole states proceeded along the lines discussed above and the results are shown in Table 2.

Considering firstly the results for nitrogen, with the exception of the limited basis set HF 4.31G and STO 4.31G calculations with unoptimized exponents (viz. exponents appropriate to the neutral molecule), it is clear that a significant decrease in bond length is computed in going from the neutral molecule to the hole state. With valence exponents appropriate to the equivalent core species (e.g. O for the nitrogen with the core electron deficit) the limited basis set calculations are in good overall agreement with the triple zeta basis set results. This is also clear for the equivalent core species (NO^+) itself where experimental data are available for direct comparison. The virtues of using computationally inexpensive basis sets (at the 4.31G level) where for the core ionized species partial optimization of exponents is accomplished by taking cognizance of the equivalent cores concept, has previously been discussed in relation to absolute binding energies [4, 14]. The work described here would strongly suggest that the approach is also successful in describing changes in bond lengths and force constants (see later) accompanying core ionizations. It may be noted that the calculations consistently suggest that the bond length for the hole state is somewhat greater than for the equivalent core species.

For the C_{1s} and O_{1s} hole states of CO an interesting picture emerges in that the calculations (independent of basis set) predict a decrease in bond length for the former and an increase for the latter with respect to the neutral molecule. The results for the small basis set calculations with optimized exponents are in very good overall agreement with the triple zeta basis set calculations. In this connection it is interesting to note that in general the "optimized" small basis set calculations are in better overall agreement with the triple zeta calculations than are those from the double zeta basis set. This can almost certainly be traced to restrictions imposed by allowing only the coefficients to be determined variationally for systems which are strongly perturbed with respect to the ground state species and for which the exponents are essentially optimized.

The calculations again indicate (the sole exception being those for the double zeta basis set pertaining to the C_{1s} hole state) that the computed equilibrium geometries for the hole states are consistently larger than those for the equivalent cores species. The comparisons for the small basis set calculations refer in each case to the "optimized" exponents for the hole state species. This is of some importance in discussing vibrational effects accompanying core ionization as will become apparent in a later section. The discussion thus far should emphasise that limited basis set calculations provide a good description of changes in bond

Table 3. Interpolated values of 2*s* and 2*p* best atom exponents as a function of "apparent" atomic number

Apparent atomic number	2*s* Exponent	2*p* Exponent
6.0	1.6083	1.5679
6.2	1.670	1.640
6.4	1.735	1.705
6.6	1.800	1.772
6.8	1.862	1.840
6.9	1.896	1.872
7.0	1.9237	1.9170
7.1	1.960	1.940
7.2	1.992	1.975
7.4	2.058	2.040
7.6	2.120	2.104
7.8	2.185	2.170
7.9	2.216	2.201
8.0	2.2458	2.2266
8.1	2.280	2.270
8.2	2.310	2.300
8.4	2.375	2.365
8.6	2.440	2.430
8.8	2.501	2.496
8.9	2.533	2.527
9.0	2.5638	2.5500
9.1	2.598	2.591

length accompanying photoionization *provided* that for the core ionized species valence exponents appropriate to the equivalent core species are employed. If this "partial optimization" of exponents is not invoked then bond length changes in general are typically predicted to be an order of magnitude too small and may also have the wrong sign. This is also clearly evident from recently published data [15].

To shed further light on this point we have investigated the relevant core hole states with STO 4.31G basis sets in which the "best atom valence exponents" employed for the atom on which the core hole is located, have been varied. A plot of the best atom valence exponents [11] for carbon, nitrogen, oxygen and fluorine versus the atomic number allows a straightforward interpolation of the 2*s* and 2*p* exponents as a function of "apparent" atomic number. The values determined in this way are displayed in Table 3. The absolute binding energies were then computed as energy differences between ground states and relevant hole states. For the former, neutral best atom exponents were used [11] whilst for the latter the 2*s* and 2*p* exponents were varied as a function of the "apparent" atomic number as indicated in Table 3. Since the 2*s* and 2*p* exponents were both systematically varied whilst the exponents for the core orbitals were unchanged, we would not necessarily expect to obtain minima for the binding energies computed as energy differences. Indeed the results displayed in Fig. 1 clearly illustrates this. The important conclusion to be reached from such a study, however, is that for these small basis sets, in each case the calculated absolute binding energies with the valence exponents for the atom on which the core hole is located close to those appropriate to the equivalent cores species, are in close agreement with the experimentally determined values.

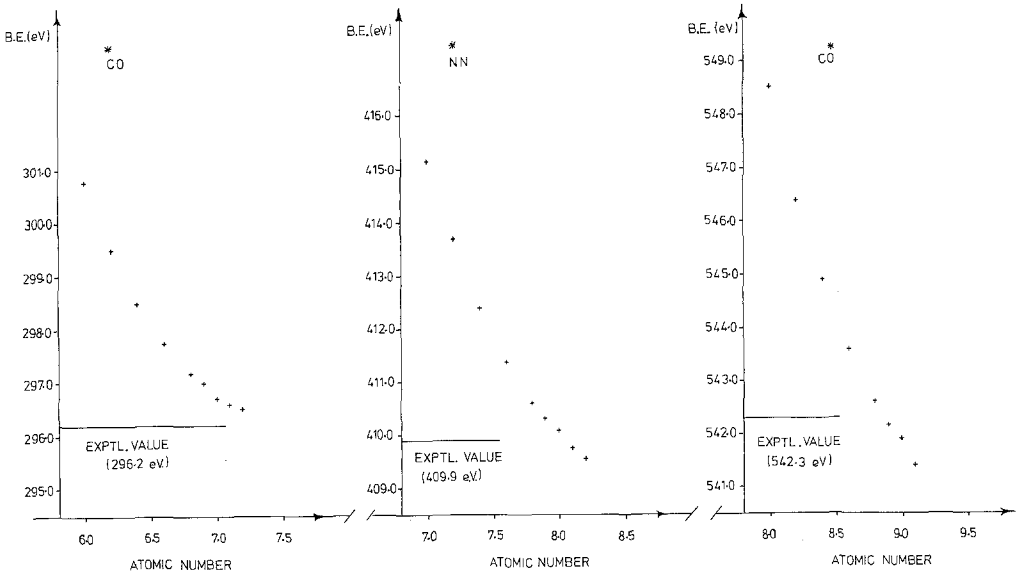


Fig. 1. Plot of calculated (ΔSCF) binding energies for the core levels of CO and N_2 as a function of the valence exponents for the hole state species

For this reason and because of computational expense the detailed investigation of potential energy curves to obtain force constants was restricted to the "optimized" STO 4.31G and triple zeta basis sets. The derived force constants for both neutral molecules, core ionized and equivalent cores species are shown in Tables 1 and 2.

Considering firstly the data corresponding to nitrogen, the computed decrease in equilibrium bond length for the core ionized species is seen to be accompanied by a relatively small change in force constant. Comparison of the triple zeta basis set calculations would suggest that the force constants for the hole state and equivalent cores species are essentially the same.

The situation with regard to carbon monoxide however is more complex. For the carbon 1*s* hole state, the decrease in bond length is accompanied by the expected increase in force constant, with the potential curves being closely similar to that for the equivalent cores species. For the O_{1s} hole state the potential energy well is considerably broader indicative of a greatly reduced force constant with respect to the neutral molecule.

These calculations overall would suggest therefore that to a first approximation changes in bond length and force constants in going from a neutral molecule to a given hole state are adequately described by considering the equivalent cores species. Depending therefore on whether there is a decrease or an increase in equilibrium bond length in going from the neutral molecule to a given core hole state, the equivalent core model provides either an upper or lower bound respectively to the change in bond lengths and in each case provides a lower bound to the force constant.

3.2. Binding Energies and Relaxation Energies

In previous papers we have systematically investigated the basis set dependencies of core binding energies and shifts from calculations on the relevant neutral molecules, core hole states and isodesmic reactions involved in the equivalent cores model [16]. We have also studied in some detail relaxation energies for core ionizations as a function of the core level and of electronic structure [4].

The simplicity of the systems studied in the present investigation allows a further dimension to be added namely an investigation of changes in relaxation energy as a function of change in geometry.

These calculations allow a comprehensive analysis of both vertical and adiabatic core binding energies as a function of basis set and theoretical model. The results are given in Tables 4 and 5, and binding energies have been computed as energy differences between ground state and hole states, from Koopmans' Theorem [17] and from an average of the relevant orbital energies for the neutral molecule and hole states, which we refer to as *relaxed Koopmans' values* [18].

Considering firstly the data pertaining to nitrogen, it is clear that the calculated absolute binding energies are in good agreement with the experimental data provided a sufficiently flexible basis set is employed. The relaxed Koopmans' values closely parallel those derived from the hole state calculations as might have been expected. The calculated "adiabatic" binding energies are virtually identical to the

Table 4. Calculated core binding energies for N_2[a]

	N_{1s} Binding Energy (eV)[c]			
Basis Set	Model[b]	Vertical (1)	Vertical (2)	Adiabatic
STO 4.31G	K	427.4	427.6	—
	Kr	415.1	415.1	415.1
	Δ	415.1	415.1	415.1
STO 4.31G (Opt.)	K	—	—	—
	Kr	411.8	411.8	411.9
	Δ	410.1	410.2	410.1
HF 4.31G	K	427.4	427.4	—
	Kr	414.4	414.3	414.3
	Δ	414.3	414.3	414.3
HF 4.31G (Opt.)	K	—	—	—
	Kr	410.4	410.5	410.4
	Δ	410.9	410.9	410.9
Double Zeta	K	428.6	428.7	—
	Kr	411.7	411.7	411.7
	Δ	412.6	412.6	412.6
Double Zeta (Opt.)	K	—	—	—
	Kr	411.8	411.8	411.8
	Δ	412.6	412.6	412.6
Triple Zeta	K	427.4	427.2	—
	Kr	410.0	409.9	410.0
	Δ	410.9	410.8	410.8

[a] Experimental value = 409.9 eV (Ref. [3]).

[b] K refers to Koopmans' Theorem.
Kr refers to Relaxed Koopmans' Theorem viz. $\frac{1}{2}(\varepsilon+\varepsilon^*)$.
Δ refers to ΔSCF calculations.

[c] Vertical (1) and Vertical (2) refer to binding energies calculated at the experimental and theoretically optimised equilibrium geometry of the ground state respectively.
Adiabatic refers to binding energies calculated as energy differences for the theoretically optimised ground state and hole state geometries.

vertical values and this is of some relevance when we come to discuss the vibrational effects accompanying core ionizations.

It is interesting to note that with a medium size basis set (double zeta) the use of valence exponents appropriate to the equivalent core species for the core ionized system fortuitously leads to calculated core binding energies in almost exact agreement with those calculated using best atom exponents appropriate to the neutral atom, with neither being in particularly good agreement with experiment. This may be attributed to the mutual interaction between the two types of variational parameters viz. the coefficients and exponents.

A similar situation obtains for carbon monoxide with the results for the "optimized" small basis sets being comparable with those for the triple zeta basis sets. The substantial shortening of the bond length in going to the carbon 1*s* hole state is reflected in the significant differences that are apparent in the adiabatic and vertical calculated binding energies. It is interesting to note that for the double

Table 5. Calculated core binding energies for CO[a]

		C_{1s} Binding Energy (eV)[c]			O_{1s} Binding Energy (eV)		
Basis Set	Model[b]	Vertical (1)	Vertical (2)	Adiabatic	Vertical (1)	Vertical (2)	Adiabatic
STO 4.31G	K	309.1	309.2	—	564.5	564.5	—
	Kr	300.8	300.9	300.9	548.6	548.5	548.2
	Δ	300.8	300.9	300.8	548.5	548.4	548.2
STO 4.31G (Opt.)	K	—	—	—	—	—	—
	Kr	298.0	297.8	297.7	544.8	544.7	544.5
	Δ	296.7	296.9	296.6	541.9	541.9	541.8
HF 4.31G	K	310.6	310.8	—	562.0	562.0	—
	Kr	302.1	302.2	302.2	545.3	545.1	544.5
	Δ	302.0	302.0	302.0	544.9	544.8	544.4
HF 4.31G (Opt.)	K	—	—	—	—	—	—
	Kr	298.3	298.4	298.3	540.9	540.7	540.4
	Δ	298.1	298.3	298.0	541.6	541.5	541.1
Double Zeta	K	311.0	311.1	—	563.7	563.7	—
	Kr	298.8	298.9	298.7	542.6	542.5	542.0
	Δ	299.6	299.7	299.5	543.3	543.2	542.9
Double Zeta (Opt.)	K	—	—	—	—	—	—
	Kr	299.0	299.1	299.0	542.6	542.5	541.8
	Δ	299.8	299.9	299.8	542.8	542.7	542.4
Triple Zeta	K	310.0	310.0	—	562.8	562.8	—
	Kr	297.3	297.2	297.0	541.3	541.4	541.0
	Δ	298.1	298.1	297.8	542.0	542.0	541.9

[a] Experimental values for C_{1s} and O_{1s} holes are 296.2 eV and 542.3 eV respectively (19).

[b] K refers to Koopmans' Theorem.
Kr refers to Relaxed Koopmans' Theorem viz. $\frac{1}{2}(\varepsilon+\varepsilon^*)$.
Δ refers to ΔSCF calculations.

[c] Vertical (1) and Vertical (2) refer to binding energies calculated at the experimental and theoretically optimised equilibrium geometry of the ground state respectively.
Adiabatic refers to binding energies calculated as energy differences for the theoretically optimised ground state and hole state geometries.

zeta basis sets the use of the equivalent core valence exponents yields slightly better results for the O_{1s} hole and slightly worse for the C_{1s} hole than employing the neutral best atom exponents. This is not unexpected on the basis of the data previously discussed for the nitrogen core hole.

The calculated relaxation energies for the N_{1s}, C_{1s} and O_{1s} core levels as a function of basis set are shown in Fig. 2. In each case the calculations refer to the experimentally determined equilibrium geometries of the neutral molecules. A striking feature of this data is the fact that the "optimized" small basis set calculations give absolute values for the relaxation energies in good agreement with those calculated with extended basis sets. Although the small "unoptimized" basis sets characteristically underestimate the total relaxation energy as has been previously pointed out [4], the trends in relaxation energies are well reproduced by comparison with the extended basis set calculations. Thus the slopes of the relaxation energy vs. change in atomic number are 4.3, 4.2, 4.6, 4.7, 4.6 and 4.6 for

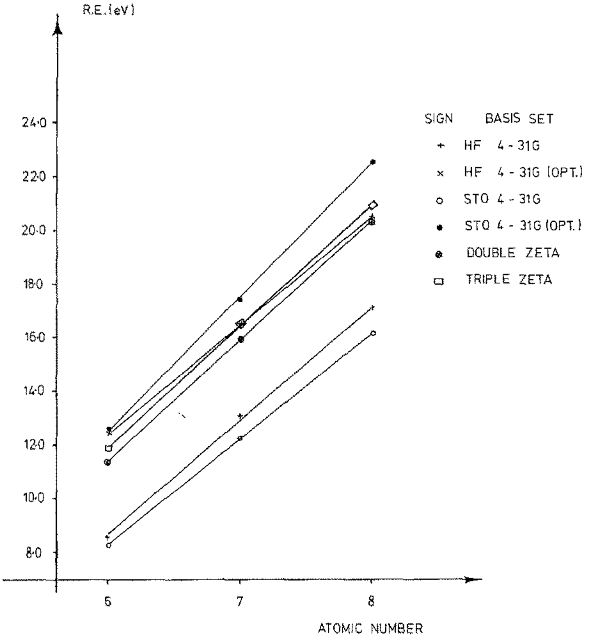


Fig. 2. Plot of calculated relaxation energies as a function of basis set versus the atomic number of the element on which the core hole is localized

HF 4.31G, HF 4.31 G (opt.), STO 4.31G, STO 4.31G (opt.), double zeta and triple zeta basis respectively. This reinforces our earlier conclusion [4] that whilst absolute values of relaxation energies are markedly basis set dependent, differences in relaxation energies are relatively insensitive to the basis set employed.

It is of some interest also to consider changes in relaxation energies as a function of the internuclear distance for the hole states considered in this work. Detailed investigations of this particular aspect have been carried out with double zeta quality basis sets and the results are displayed in Fig. 3, where the reference in each case is with respect to the theoretically calculated equilibrium geometries for the neutral molecules. For these closely related systems for the C_{1s}, N_{1s} and O_{1s} holes the changes in relaxation energies are linear functions of the change in bond length with positive slopes (viz. relaxation energy increases with increasing bond length). It is clear however that in each case the changes in relaxation energies represent a small fraction of the total relaxation energies. The order of increasing slope of $C_{1s} < N_{1s} < O_{1s}$ follows the order of increasing total relaxation energies.

3.3. Density Contour Analysis of Electronic Reorganizations Accompanying Core Ionization

In previous papers we have discussed the valence electronic relaxations accompanying core electron photoionization in terms of both crude Mulliken population analyses and by means of density difference contours [4, 16, 20]. Whilst a consideration of population analyses can provide a valuable qualitative

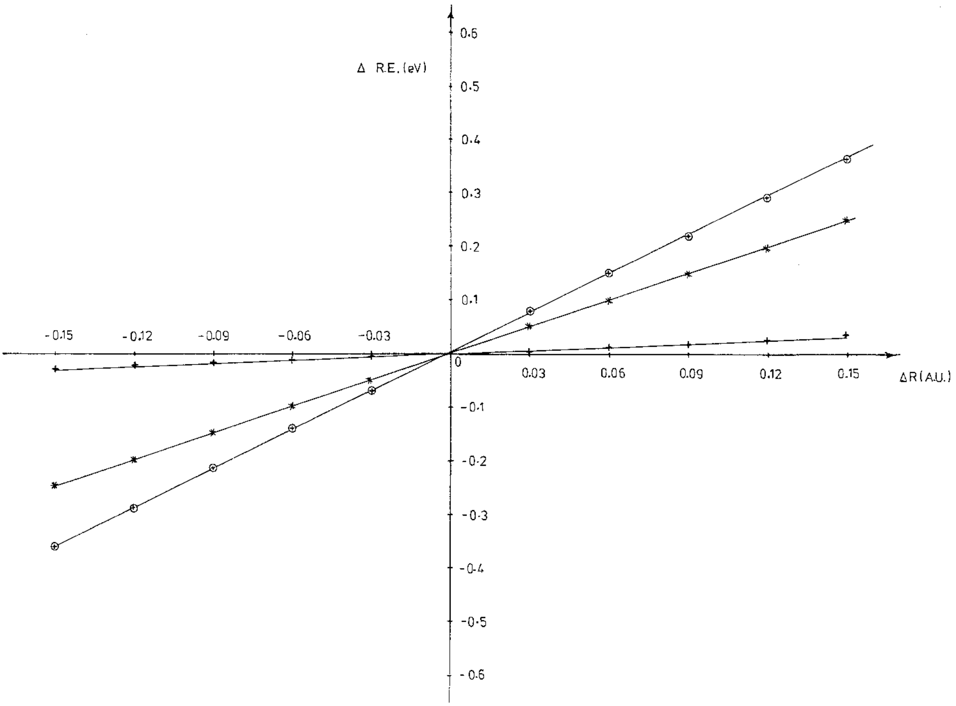
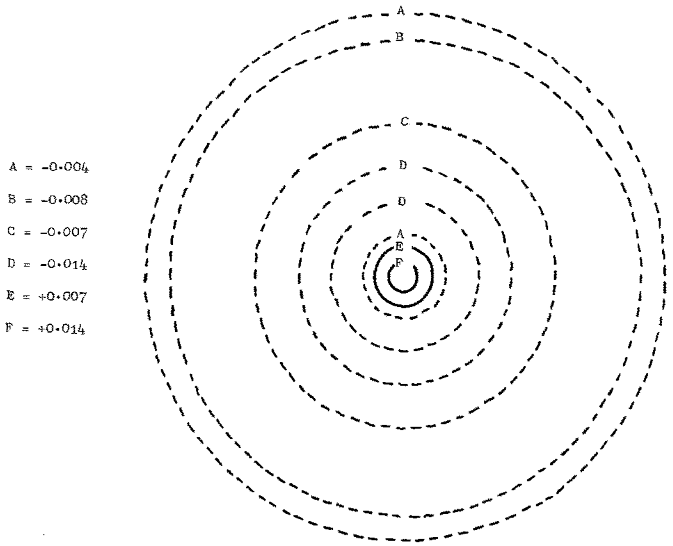


Fig. 3. Plot of differences of relaxation energies for N_2 and CO versus internuclear distance.

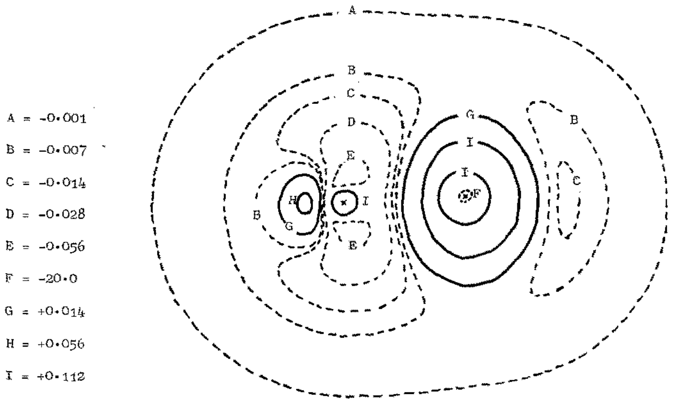
⊕ refers to $C\overset{*}{O}$ species
* refers to $N\overset{*}{N}$ species
+ refers to $\overset{*}{C}O$ species
(see text)

picture of the substantial migrations in electron densities which occur on core ionization, the computationally more expensive analyses in terms of detailed density difference contour maps are even more revealing, since they provide a three dimensional picture of the relaxation phenomena. This has recently been demonstrated most effectively by Streitweiser and coworkers [21], in the particular case of the C_{1s} and O_{1s} hole states of CO. Unfortunately the contours produced make it difficult to appreciate the substantial reorganizations of the electronic charge distribution in the bonding regions which are obviously of some considerable importance in discussing vibrational effects for the core hole states. In the present work density difference contours have been constructed using the ATMOL program package for analysis of molecular wavefunctions, and employing a double zeta basis set.

The areas studied were in each case divided into a mesh of 97 × 97 points, and the derived density difference grid was then used to compute the appropriate density difference contours. In computing the density difference contours the same geometries were used for both the ground state and relevant core hole states; these geometries corresponding in each case to those appropriate to the calculated

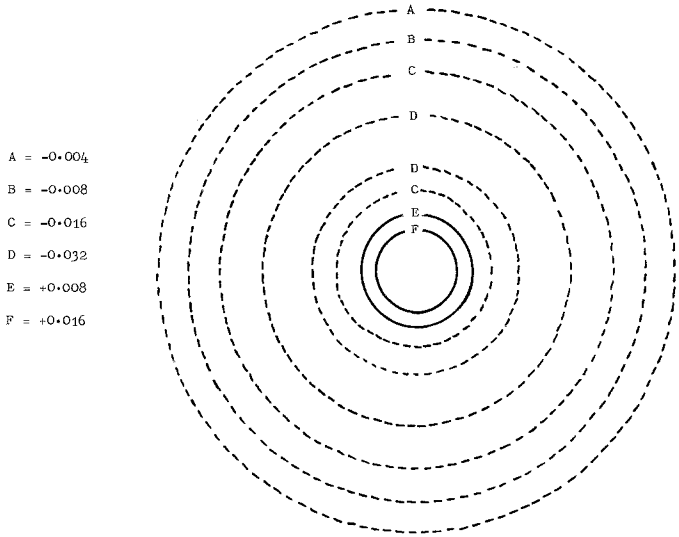


(N$\overset{*}{N}$) - (NN) MOLECULAR PLANE

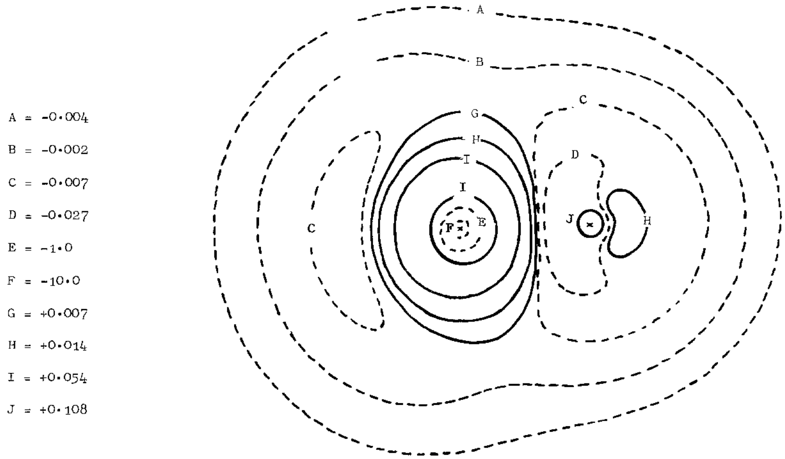


4a (N$\overset{*}{N}$) - (NN) PLANE ⊥ THROUGH THE CENTRE

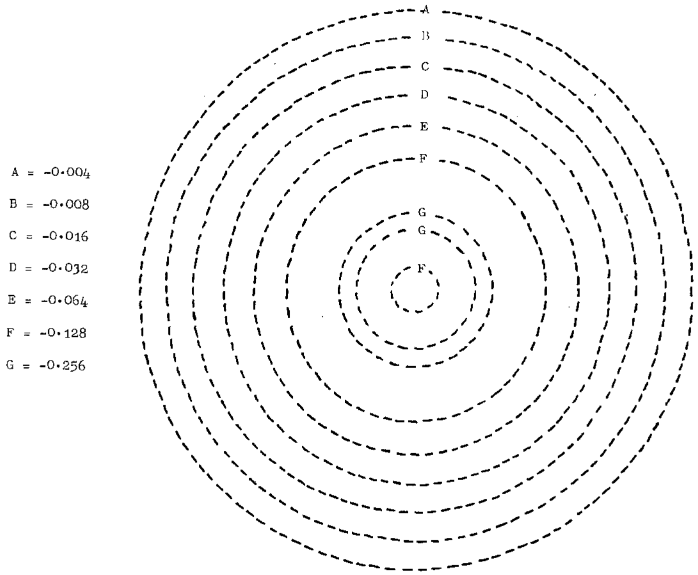
Figs. 4a, 4b, and 4c. Electron density difference contours for the hole states of N_2 and CO with respect to the neutral molecules. (The solid contours indicate an increase and the dotted a decrease in density in going from the neutral molecule to the hole state and the markers "X" indicate the positions of the nuclei.) Contours are given in units of (electron/Bohr^3)



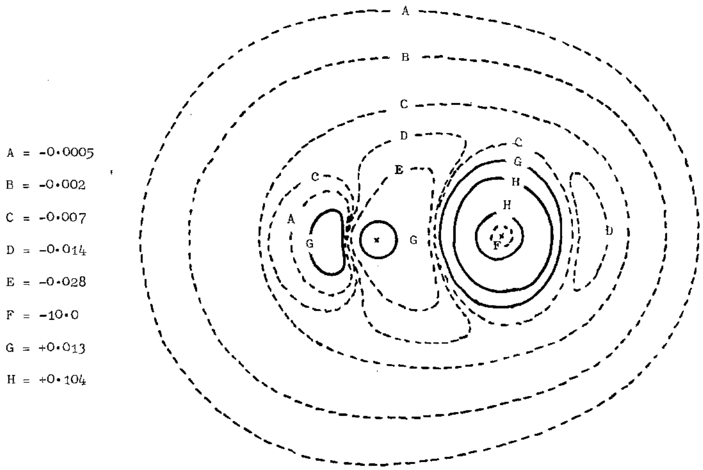
($\overset{*}{\mathrm{C}}$ O)-(C O) PLANE ⊥ THROUGH THE CENTRE



4b ($\overset{*}{\mathrm{C}}$ O) - (C O) MOLECULAR PLANE



$(C\overset{*}{O})-(CO)$ PLANE ⊥ THROUGH THE CENTRE



4c

$(C\overset{*}{O})-(CO)$ MOLECULAR PLANE equilibrium geometries of the neutral molecules using a double zeta basis set (2.082 a.u. for N_2 and 2.155 a.u. for CO).

The planes chosen most effectively to illustrate the relaxation phenomena are the molecular (XY) plane covering an area of 10×10 a.u. and the plane perpendicular to the molecular axis bisecting the molecule. This plane covered an area of 8×8 a.u.

The results for the N_{1s} core hole in N_2 and for the C_{1s} and O_{1s} holes in CO are presented in Figs. 4a, 4b and 4c. In each case the solid lines correspond to an increase and the dotted contours to a decrease in density on going from the neutral molecule to the hole state.

Considering firstly the contours for the molecular planes, the extensive migration of electron density to the vicinity of the atom on which the core hole is located is clearly evident. It is also clear that there is a very substantial overall spatial contraction of the electron distribution in going from the neutral molecule to the core hole state. That this arises largely from electronic reorganizations of the valence electrons may most readily be inferred by reference to the contours in the immediate vicinity of the nuclei. It is clear that for the atom on which the core hole is located there is a decrease in electron density in this region which contrasts sharply with the large increase in electron density in the region appropriate to the valence electron distribution. Along the internuclear axes the contours corresponding to the molecular plane show that there are substantial changes in electron density with an overall increase in the region close to the nucleus on which the core hole is located and a decrease towards the other atom. The planes perpendicular to and bisecting the molecular axes are particularly revealing in this respect since they show for both the N_{1s} and C_{1s} holes a substantial increase in electron density in the bonding region whilst for the O_{1s} hole there is an overall decrease. These contours therefore provide a simple pictorial rationalization for the driving force behind the decrease in bond length accompanying N_{1s} and C_{1s} core ionization in N_2 and CO respectively and the increase in bond length in going to the O_{1s} core hole state for the latter.

3.4. Vibrational Fine Structure Accompanying Core Ionizations

In the previous sections we have shown that the equilibrium geometries for the core ionized species of N_2 and CO are significantly different from those of the neutral molecules and more particularly the potential energy surfaces for the ionized species reveal substantial changes in force constants.

The development of a high resolution spectrometer incorporating the fine focusing X-ray monochromatization scheme has revealed significant fine structure in the main core photoionization peaks for N_2 and CO which had previously gone undetected [1–3]. An elegant discussion of the interpretation of this fine structure in terms of vibrational excitations accompanying core ionizations has been presented by Siegbahn and coworkers [2, 3]. As we have previously pointed out, however, it is not entirely clear in the absence of a detailed theoretical examination that force constants derived for the equivalent core species will be entirely adequate in discussing this data. The detailed analysis presented in Sect. 3.1 indicates that the potential energy surface for the equivalent cores species form a reasonable basis for the semi-quantitative discussion of the vibrational effects. However two differences were apparent with respect to the hole state species themselves. Firstly as we have previously mentioned, depending on whether there is a decrease or an increase in equilibrium bond length in going from the neutral molecule to a given core hole state, the equivalent cores model provides either an upper or lower bound respectively to these changes in bond length. Secondly, the force constants for the equivalent cores species are consistently smaller than those for the corresponding hole states such that the separation between the vibrational levels is almost certainly underestimated. Thus for the C_{1s} hole state of CO and the N_{1s} hole state of N_2, Siegbahn and coworkers [3] obtained an excellent fit to the observed asymmetric line shapes by computing the relevant Franck Condon factors taking separations between the vibrational energy levels of 0.29 eV and changes in bond lengths inferred from the equivalent cores species (NO^+). The theoretical calculations detailed in the discussion in the previous section, however, suggest vibrational frequencies of 0.33 eV for the C_{1s} and N_{1s} hole states of CO and N_2 respectively. A further point of interest is clearly an examination of the corresponding vibrational effects accompanying core ionization of the O_{1s} level in CO for which there appears to have been no previous detailed theoretical examination, and for which high resolution experimental data have only recently become available. The calculated vibrational frequency for the core ionized species in this case is substantially lower (0.22 eV) than for the other holes.

The discussion to be presented below is within the harmonic approximation and since it will become apparent that vibrational excitations for the ionized states are restricted at normal temperatures to the lowest few levels we may briefly consider the possible importance of anharmonicities for these levels. As a model we may consider the ground state of CO for which experimental data of a high order of accuracy are well documented [22]. For example the change in vibrational separation in going from the $0 \rightarrow 1$ to the $5 \rightarrow 6$ transition amounts to less than 4% (0.26 eV vs. 0.25 eV). Since the interpretation of the unresolved ESCA data essentially involves a detailed lineshape analysis, such small changes in vibrational separations arising from anharmonicity corrections may reasonably be ignored. The effects of any slight anharmonicity would be expected to be even less in respect of the calculated Franck Condon factors, which were computed using the recurrence relations derived by Ansbacher [23].

In this investigation we have addressed ourselves to the following points:

(1) The computation of the vibrational envelope for core ionizations in N_2 and CO from the theoretically calculated energy separations and Franck-Condon factors, derived from calculations at the triple zeta level. This enables a detailed comparison to be made with the corresponding analysis previously presented [3] which is based solely on experimental data, and also allows an extension to be made to a consideration of vibrational effects for the O_{1s} hole state in CO.

(2) Consequent upon the interpretation of the fine structure accompanying core ionization in these systems as arising from vibrational effects, to investigate the temperature dependence of the overall band profiles.

In the interpretation of the experimental data only transitions involving the ground state ($v''=0$) of CO and N_2 need be considered (the effect of temperature on band profile will be considered in a later section).

3.4.1. Nitrogen Molecule

The distinct asymmetry of the direct photoionization peak for the core levels of nitrogen has been interpreted by Siegbahn and coworkers [3] in terms of excitation to the two lowest vibrational levels of the hole state. It is evident from the comparison between the theoretical analysis presented here and the experimental data that higher excitation must be involved. Taking the individual component linewidths obtained from Siegbahn's analysis (FWHM[1] 0.37 eV) together with the theoretically computed vibrational energy separations, an improved fit may be obtained to the experimental envelope. The derived Franck-Condon factors for the $v''=0$ to $v'=0$, 1, 2 are 80%, 19% and 1% respectively. A more critical test for the calculations however is to take the theoretically derived change in bond length in conjunction with the vibrational separation to compute the relevant Franck-Condon factors. We have taken the experimental band profile together with the theoretically calculated energy separations and Franck-Condon factors and obtained almost exact agreement, using as the only variable the FWHM of the individual components. The relevant data are displayed in Fig. 5, the derived "best fit" FWHM of 0.39 eV of the individual components being in excellent agreement with that derived from the previous analysis. This solely theoretical analysis differs from that based on the equivalent cores analysis primarily in terms of the somewhat lower overall contributions of the higher vibrational excitations.

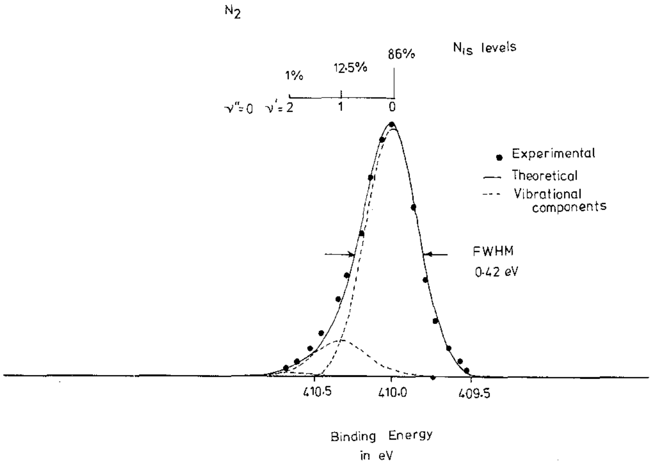


Fig. 5. The N_{1s} spectrum of nitrogen molecule showing three vibrational components of FWHM = 0.39 eV separated by 0.33 eV

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[1] FWHM: Full Width at Half Maximum.

3.4.2. Carbon Monoxide

3.4.2.a C_{1s} Levels

A similar analysis to that presented for nitrogen has been carried out for CO. Thus using the individual component FWHM derived by Siegbahn (0.48 eV) we have taken our theoretically calculated energy separation (0.33 eV) and again an improved fit may be obtained to the experimental data. This analysis reveals that the large change in bond length is accompanied by the excitation of up to five vibrational quanta and the derived Franck-Condon factors for the $v''=0$ to $v'=0$, 1, 2, 3, 4 transitions are 36%, 36%, 20%, 7% and 1% respectively. Again the more critical test of the theory is by direct comparison of a solely theoretically based analysis with the experimental band profile. The quantitative nature of such an analysis is clearly evident from the data displayed in Fig. 6, the derived FWHM for the individual component of 0.54 eV is again in good agreement with that derived from the equivalent cores analysis. Before an analysis of the vibrational effects accompanying core ionization of the O_{1s} level in carbon monoxide is presented we may briefly consider some previously published high resolution spectra [1] for carbon monoxide since these provide the only experimental criteria currently available in the literature for direct comparison with the theoretical analysis. The published high resolution data pertaining to the C_{1s} levels of carbon monoxide discussed thus far [3] refer to a lower instrumental resolution than that for nitrogen (e.g. FWHM for individual components 0.54 eV versus 0.39 eV from the analysis presented here). However, in an earlier paper [1] in which a detailed description of the high resolution ESCA instrument employing a fine focussed X-ray monochromator was described, core level spectra for carbon monoxide were reported with composite linewidths of 0.65 eV and 0.52 eV for the C_{1s} and O_{1s} levels respectively. Unfortunately the energy scale on which this data is

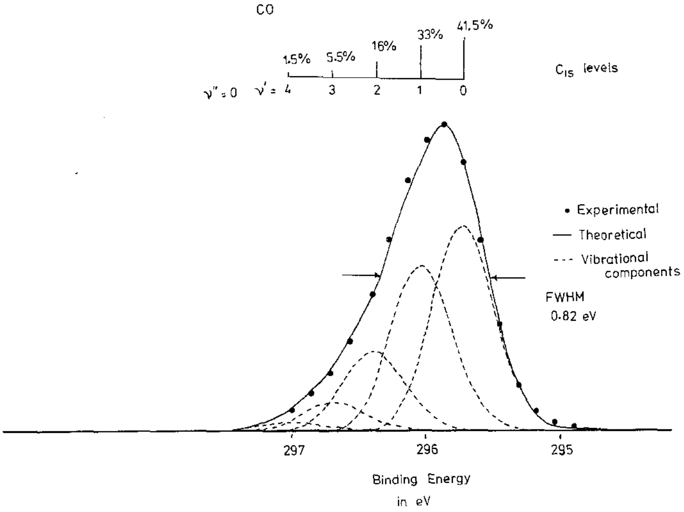

Fig. 6. The C_{1s} spectrum of carbon monoxide showing five vibrational components with FWHM = 0.54 eV separated by 0.33 eV

recorded in the literature is such that a detailed examination of the asymmetry of the band envelope is not feasible (energy scale 2.67 mm/eV C_{1s} levels, 3.33 mm/eV O_{1s} levels). We have, therefore, taken our theoretically derived analysis for the C_{1s} levels as previously described and systematically varied the component linewidths to fit the published FWHM for the higher resolution spectrum (0.65 eV). The FWHM for the individual components derived from this analysis is 0.32 eV in good agreement with that derived from the analysis of the nitrogen spectrum (FWHM = 0.39 eV) and that pertaining to Neon (FWHM = 0.39 eV) measured at comparable instrumental resolution [1–3]. The theoretically simulated spectra for the C_{1s} levels corresponding to this higher resolution are shown in Fig. 7 where the data have been plotted on energy scales corresponding both to the published data and to that employed in the previous figures. Comparison of the theoretically calculated composite band profile and the higher resolution experimental data shows them to be in excellent overall agreement.

3.4.2.b O_{1s} Levels

As we have previously noted, vibrational effects accompanying core ionization of the O_{1s} level in carbon monoxide are of particular interest since no detailed analysis has previously been presented. This situation may be attributed in part to the lack of experimental data pertaining to the equivalent core species namely CF^+. Whilst this work was essentially complete and in the process of being written up, a paper by Doncke and Cederbaum [24] appeared which briefly considered vibrational effects accompanying core ionization of both the C_{1s} and O_{1s} levels of carbon monoxide employing a many body formalism using Green's functions. Whilst their analysis of the C_{1s} vibrational envelope corresponds reasonably closely to that presented here, the fact that the O_{1s} core ionized state has an equilibrium bond length somewhat greater than that of the neutral molecule leads

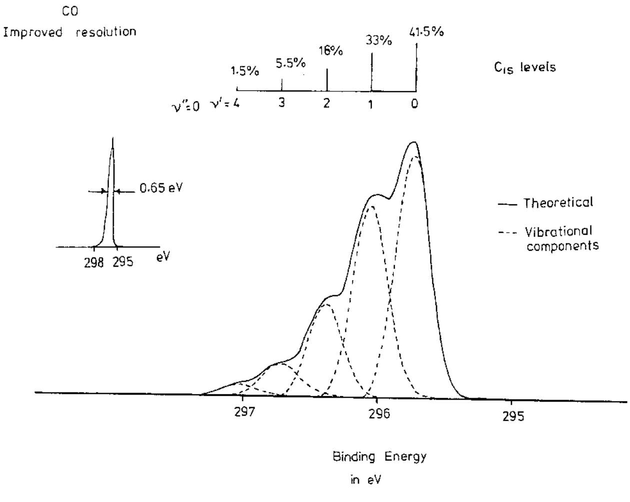

Fig. 7. Theoretically simulated C_{1s} spectra of carbon monoxide on a large and a small energy scale. The individual vibrational components have FWHM = 0.32 eV and are separated by 0.33 eV. Composite linewidth of the peak is 0.65 eV

to a divergent situation in the many body approach. It was, therefore, not possible to investigate in detail any vibrational effects, for the O_{1s} hole state, however the authors conclude that "the O_{1s} electron is strictly non-bonding in the one particle approximation" and state that "this is in qualitative agreement with the ESCA spectrum of CO which shows no detectable broadening". The detailed analyses which we present below indicate that both of these conclusions are in error and that significant vibrational effects are predicted and may in fact be inferred from the available experimental data.

The theoretical calculations detailed in the previous section show that the force constant for the O_{1s} hole state of CO is substantially smaller than that for the neutral molecule, which accords with the increased bond length in going to the core ionized species. Taking the force constants and change in bond length derived from the theoretical analysis the energy separations and Franck-Condon factors may readily be computed. In order to simulate the vibrational envelope for the O_{1s} level an estimate of the FWHM for each component is required. The available data in the literature from the high resolution gas phase studies indicate that the composite linewidth associated with the 1*s* levels of first row atoms is C, ~0.32 eV[2]; N, 0.39 eV[2]; Ne, 0.39 eV [1–3]. It should be emphasized that these linewidths are largely determined by the instrumental contributions (X-ray source, analyzer etc.) since it is known that the natural linewidths are considerably smaller [1–3]. It is clear that the linewidth appropriate to the same instrumental resolution for the O_{1s} level should therefore be ~0.39 eV. The highest resolution data for carbon monoxide show that when the composite linewidth for the C_{1s} levels is ~0.65 eV that for the O_{1s} levels is ~0.52 eV [1]. The significantly broadened peak for the O_{1s} levels may therefore be taken as prima facia experimental

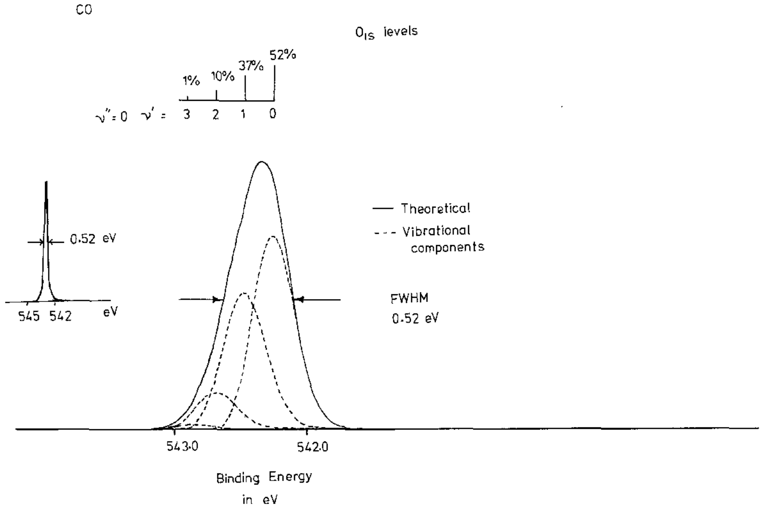

Fig. 8. Theoretically simulated O_{1s} spectra of carbon monoxide on a large and a small energy scale. The four vibrational components have FWHM = 0.39 eV and are separated by 0.22 eV

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[2] These values for the C_{1s} and N_{1s} levels are those derived from the theoretical analysis of the experimental data as described above.

evidence for vibrational effects. Taking a FWHM of 0.39 eV for the individual components, the calculated FWHM for the composite spectrum derived from the theoretical analysis is 0.52 eV in complete agreement with the experimental data. Unfortunately the published data is too compressed to clearly show the marked asymmetry of the O_{1s} core level, so that the only experimental parameter available is the total FWHM. Fig. 8 however, which has been plotted on a comparable scale to that for the expanded C_{1s} spectrum clearly shows the vibrational effects which should be evident in an expanded experimental spectrum of the O_{1s} levels. The fact that the O_{1s} spectrum of CO has a smaller FWHM than the C_{1s} spectrum and that the latter is more asymmetric stems mainly from the fact that the individual vibrational components in the O_{1s} spectrum are more closely spaced than for either the carbon hole or for the neutral molecule. For comparison purposes the theoretically simulated O_{1s} level spectrum is also plotted in Fig. 8 on a comparable scale to that of the published data. Superposition of this spectrum with that previously publushed, shows the excellent agreement between the two.

Whilst this work was essentially complete further experimental data for the O_{1s} levels of CO became available [25] which fully substantiate this analysis. The experimental data plotted on an expanded scale (reproduced in Fig. 9) has been obtained by Siegbahn and Gelius [25] employing the fine focus X-ray monochromatization scheme. The asymmetry of the spectrum although less marked than for the C_{1s} levels is clearly apparent and the resolution of the spectrometer giving a composite linewidth of 0.66 eV corresponds to the composite linewidth of 0.82 eV for the C_{1s} levels reproduced in Fig. 6. We have therefore taken our theoretically calculated Franck-Condon factors and vibrational energy separations and obtained the best overall fit to the band profile using as the only variable the FWHM of the individual vibrational components. This fit is also indicated in Fig. 9 and is seen to be in excellent overall agreement (the minor discrepancies at

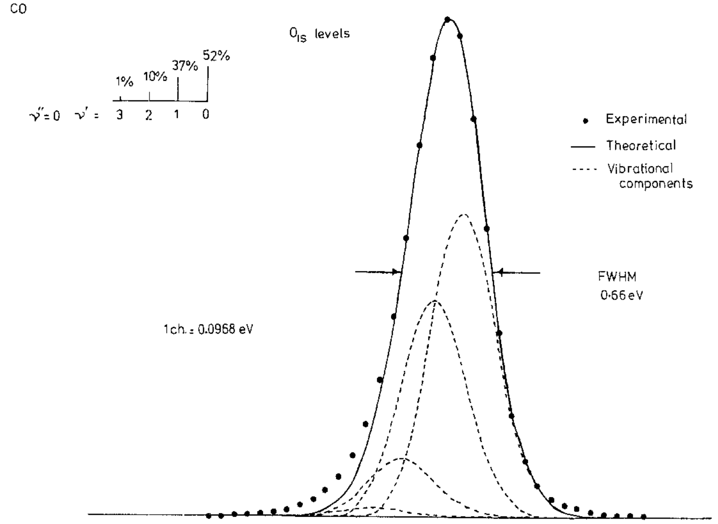

Fig. 9. The O_{1s} spectrum of carbon monoxide showing four vibrational components with FWHM = 0.58 eV separated by 0.22 eV

the leading and trailing edges may well arise from the use of purely Gaussian lineshapes since the individual components would be expected to be hybrids arising from the convultion of a Lorentzian lineshape contribution due to the inherent width of the core level and a Gaussian from the spectrometer contributions). The derived FWHM for the component peaks is 0.58 eV which is in excellent agreement with that calculated from the derived linewidths for the O_{1s} level at higher instrumental resolution (0.39 eV) and for the C_{1s} levels at the same (0.54 eV) and higher instrumental resolution (0.32 eV) based on a first-order analysis of the composite linewidths taking the inherent widths of the levels and the spectrometer contributions in simple quadrature.

3.5. Temperature Dependence of Vibrational Fine Structure Profiles

The interpretation of the band profiles for the N_{1s}, C_{1s} and O_{1s} core levels in N_2 and CO as arising from vibrational progressions involving the ground vibrational states of the neutral molecules in each case suggests that a confirmation of this assignment could be made by temperature dependent studies of the band profiles. Unfortunately the vibrational energy spacings for these molecules are such that significant population of other than the $v''=0$ level requires considerably elevated temperatures. We have restricted ourselves therefore to a theoretical analysis which would correspond to realistic experimental conditions. We have considered therefore the change in band profile for N_2 at 1800 K. The Boltzmann distribution is such that at this temperature the population of the $v''=0$ and $v''=1$ levels are $\sim 87\%$ and $\sim 13\%$ respectively. We have therefore considered the vibrational profile arising from transitions from $v''=0$ to $v'=0$, 1, 2 and from $v''=1$ to $v'=0$, 1, 2, and 3 using the theoretically calculated energy separations, force constants and change in bond length previously discussed. The results are displayed in Fig. 10. The differences with respect to the room temperature spec-

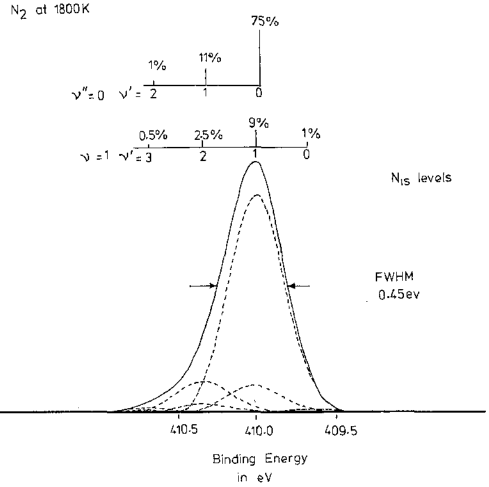

Fig. 10. Theoretically simulated N_{1s} spectrum of nitrogen molecule at 1800 K, showing vibrational excitation from the $v''=0$ and $v''=1$ levels. The individual vibrational components have FWHM = 0.39 eV. The vibrational separations being 0.33 eV

trum are small but significant and should be detectable with current instrumentation. Thus the FWHM of the high temperature spectrum should be ~0.3 eV larger than that at room temperature and the tails at higher and lower binding energies should also be observable. We have also carried out a similar analysis for the C_{1s} and O_{1s} levels of CO. However the feasibility of such high temperature experiments involving CO would almost certainly preclude such an experimental investigation so that we have not reproduced the results here.

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