Photoelectron Spectra of the Nitrosomethane, Trifluoronitrosomethane, Nitrosyl Fluoride, and Nitrosyl Chloride

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He(I) p.e. spectra, qualitative m.o. models, and semiempirical calculations are presented for the title compounds to elucidate their electronic structures. No basic differences in the bonding of these isoelectronic and isostructural molecules have been found. Changes of ionization potentials within the series are attributed to differing hyperconjugative interactions of the substituents X and NO, and the electronegativities of X. During ionization experiments the temperature-dependent decomposition of dimeric *cis*-nitrosomethane into its monomers can be observed directly.

SINCE the preparation of the first nitroso-derivatives a hundred years ago investigations of these compounds have repeatedly yielded puzzling results:[1] dimers,[2] and consequently *cis–trans* isomers,[3] are formed by *C*-nitroso-compounds under normal conditions, whilst their *C*-halogenated derivatives and halides exist as monomers. Unusually long X–N bond distances are found with electronegative X groups.[4,5] This is in contrast to bond dissociation energies: Gowenlock and his co-workers [5] showed that D(X–N) values of nitroso-compounds are generally small, but within this group of compounds the strongest bond is found in nitrosyl fluoride. Weak X–NO (X = halide) bonds were deduced from a simple valence-bond (VB) model including contributions from ionic and neutral structures, in spite of the fact that

$$\mathrm{X^- \; N{\equiv}O^+ \longleftrightarrow X{-}N{=}O \longleftrightarrow X^+ \; N{\equiv}O^-}$$

stretching force constants and i.r. bond orders favour NO double bonding as well as weak X–N bonds.[6]

The unusual properties have also stimulated several theoretical examinations of the relatively simple nitrosyl fluoride and of related molecules.[7-11] The workers agree that in NOF the fluorine atom and the NO group essentially retain their individual identities. However, *ab initio* results for NOF yield contrary F–N–O bonding descriptions. Peyerimhoff and Buenker [7] ascribed the stability of the F–N bond ‘ to the advantage gained by pairing the odd electrons of both fluorine and NO in a single molecular orbital ’ (*i.e.* the highest occupied m.o.), whereas Peslak's results [8] ‘ indicate that its stability is due to a net contribution of several m.o.s and, in fact, the highest occupied orbital is predicted to be slightly F–N antibonding ’.

For a comprehensive understanding of the properties of nitroso-compounds extensive information, experimental as well as theoretical, is necessary. As a contribution to this the photoelectron (p.e.) spectra and semi-empirical calculations of some small XNO molecules (X = Me, CF_3, F, and Cl) and comments on the bonding in these molecules are presented below.

EXPERIMENTAL

The *cis*-dimer of nitrosomethane was prepared by oxidation of *N*-methylhydroxylamine with periodic acid.[12] Dimeric *trans*-nitrosomethane was obtained by isomerization of the *cis*-dimer in hot chloroform.[12] Both compounds were identified by their melting points and i.r. spectra. To obtain the He(I) spectrum of the monomeric nitrosomethane, thermal decomposition of both dimeric species was attempted. The spectra were recorded on Perkin-Elmer PS 15 and PS 16 spectrometers equipped with exchangeable heated inlets and high-intensity lamps.

Thermal Decomposition of trans-$(MeNO)_2$.—*Internal heating*. Using the commercially available heated inlet (Perkin-Elmer), the spectrum of the *trans* isomer was obtained at room temperature.[13] The substance sublimed quickly above 30 °C. Because valves for pressure control were lacking, decomposition to monomeric nitrosomethane at higher temperature was not possible with this equipment.

External heating. For external heating an inlet was used, consisting of a stainless-steel tube, a glass reservoir for the sample, and a valve for controlling the pressure. The whole unit could be wrapped up in heating tape allowing external heating to 220 °C. Measurement of the temperature in the inside of the inlet tube was not possible, so that some variation in the temperature values (outer to inner) might be expected. With this inlet, the spectrum of dimeric *trans*-nitrosomethane was the same as achieved by internal heating. Increasing the external temperature to the limit of 220 °C did not produce the spectrum of the monomeric species.

Thermal Decomposition of cis-$(MeNO)_2$.—*Internal heating*.

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[1] (*a*) B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321; (*b*) W. Lüttke, *Z. Electrochem.*, 1957, **61**, 302; (*c*) L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, 1960, **56**, 682; (*d*) D. Coffey, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, 1968, **49**, 591.

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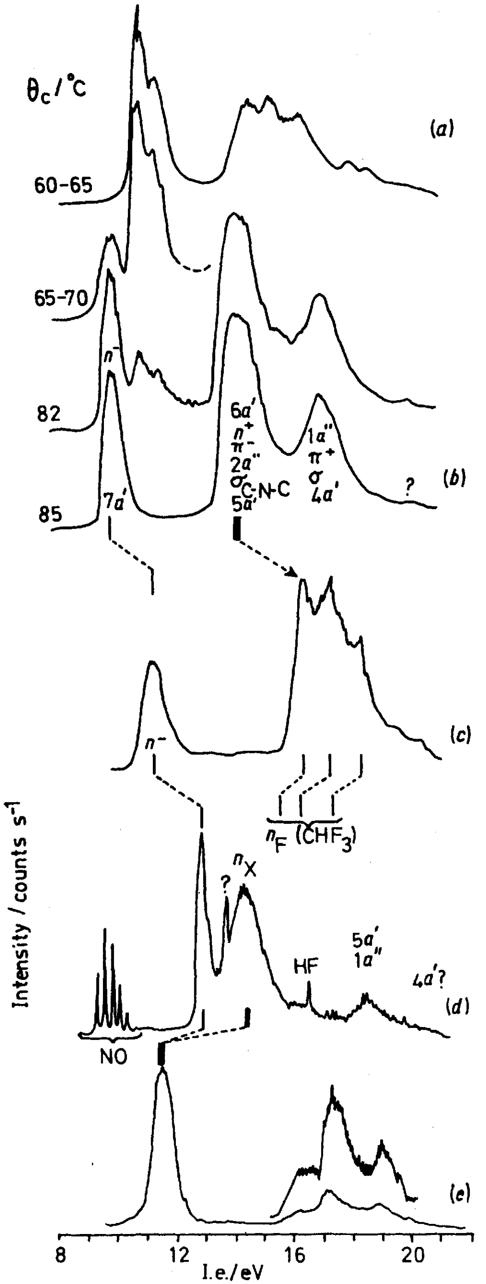

FIGURE 1 He(I) p.e. spectra of the series MeNO (*b*), CF$_3$NO (*c*), NOF (*d*), and NOCl (*e*). The temperature-dependent decomposition of *cis*-(MeNO)$_2$ (*a*) into MeNO (*b*) is displayed in the inset. The assignment is based on semiempirical calculations and simple m.o. considerations

Using the Perkin-Elmer inlet, the spectrum of the *cis*-dimer was obtained up to 65 °C [Figure 1(*a*)]. Increasing the temperature produced superimposed spectra of the *cis*-dimeric and monomeric nitrosomethanes, whereas at 84 °C the spectrum of monomeric MeNO was recorded [Figure 1(*b*)].

External heating. The inlet described above was used. Heating of only the reservoir to 80 °C produced the spectrum of dimeric nitrosomethane [Figure 1(*a*)]. Increasing the temperature of the reservoir did not change the spectrum. When the whole inlet unit was heated by the heating tape, the superimposed spectra of the dimer and the monomer, and finally the spectrum of the monomeric species, appeared between 90 and 120 °C. No further change occurred up to 220 °C.

Trifluoronitrosomethane was prepared as in ref. 14. The compounds NOF and NOCl were commercial samples. Argon was used for calibration of the p.e. spectra; the sharp p.e. bands of contaminating NO and HF rendered a further calibration of the NOF spectrum unnecessary. Structural parameters of XNO molecules were taken from refs. 4, 5, 8, and 9 and from literature quoted therein.

RESULTS AND DISCUSSION

Figure 1 shows the He(I) p.e. spectra of the nitroso-compounds MeNO (*b*), CF$_3$NO (*c*), NOF (*d*), NOCl (*e*), and in the inset the temperature-dependent decomposition of the *cis*-dimer of nitrosomethane (*a*) into the monomer (*b*). Vertical ionization potentials of the title compounds and of both *cis*- and *trans*-(MeNO)$_2$ [13] are summarized in Table 1. The assignment of the bands is included in Figure 1. CNDO eigenvalues of XNO and the parent molecules HX and HNO are correlated in Figure 2. Here, too, CNDO m.o. diagrams of MeNO and NOF are drawn to illustrate the change in X–N–O bonding types due to opposite inductive effects of the X groups. The molecules XNO possess nine (X = Me, F, or Cl) and 18 (X = CF$_3$) valence orbitals which transform as *a′* and *a″* under C_s symmetry. On energy grounds six or seven bands should appear in the He(I) regions of MeNO or X (X = halide), whereas *ca*. 13 p.e. bands are expected for CF$_3$NO.

TABLE 1

Vertical ionization potentials (band maxima) of XNO compounds and nitrosomethane dimers (±0.08 eV)

	I.e.$_1$	I.e.$_2$	I.e.$_3$	I.e.$_4$	I.e.$_5$	I.e.$_6$	I.e.$_7$
MeNO	9.70	13.9	16.3				
CF$_3$NO	11.10	16.17	17.08	18.08			
NOF	12.76	14.4	18.46				
NOCl	11.43	16.15	17.1	18.85			
cis-(MeNO)$_2$	10.61 11.74	11.14	14.25	14.93	15.95	17.5	
trans-(MeNO)$_2$	8.57	9.86	10.79 10.92	13.65	15.35	16.85	18.2

Typical π-type bonding is preserved in *a″* orbitals perpendicular to the nodal plane spread by X– or C–N–O atoms (Figure 2). However, strong mixing occurs between π- and σ-type orbitals of *a′* symmetry. They include lone-pair orbitals as well as σ_{X-N} and σ_{N-O} orbitals. Although σ–π separation of *a′* m.o.s is removed, it was useful to symbolize typical m.o.s with respect to the m.o. diagrams illustrated in Figure 2 to facilitate the discussion and the assignment. The abbreviations used are given in the Figures 1 and 2.

C-Nitroso Compounds.—Based on qualitative considerations, the first p.e. band of the monomer nitrosomethane [Figure 1(*b*)] is attributed to the n^- m.o. characterized by strong π_{NO} antibonding and weak σ_{X-N} bonding contributions; π^- and n^+ orbitals are assigned to the second band. A splitting of *ca*. 4 eV * between n^- and

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* Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J.

[14] J. Mason (Banus) and J. Dunderdale, *J. Chem. Soc.*, 1956, 754.

n^+ follows from this interpretation. This corresponds to the p.e. data of the analogous *trans*-azomethane [15] where lone-pair orbital combinations n^- and n^+ are separated by 3.3 eV. Taking into account a corresponding inductive adjustment of the splitting centre α_n, a similar energy gap between n^- and n^+ orbitals in MeNO is to be expected and was experimentally found here. Some uncertainty remains with localizing the σ_{C-N-O} energy ($5a'$) in view of the CNDO (Figure 2) and recent *ab initio* [16] results. With respect to band intensities (1 : 3 : 2 : 1?) it should be ascribed to the second band.

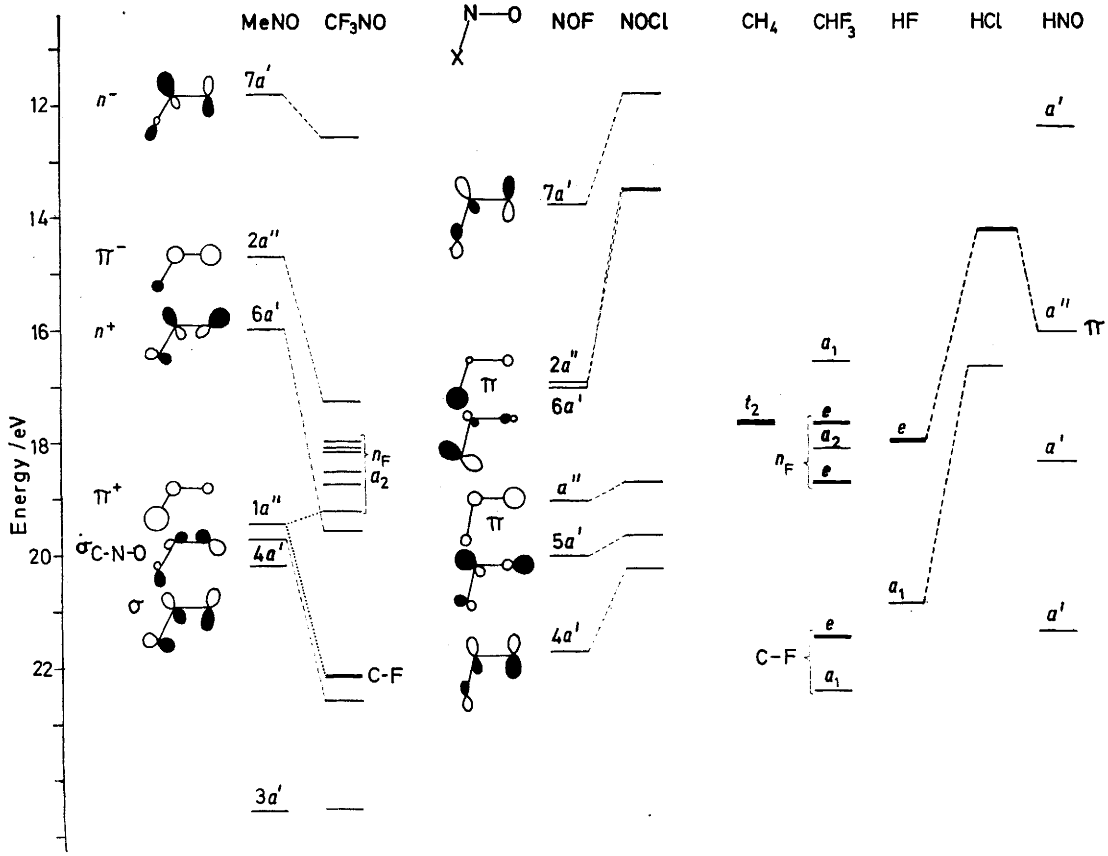

FIGURE 2 Correlation diagram of CNDO orbital energies of the XNO series (X = Me, CF_3, F, or Cl) and of the parent molecules CH_4, CHF_3, HF, HCl, and HNO. CNDO eigenfunctions for MeNO and NOF and a complete assignment of valence orbitals are also given

In order to confirm experimentally our assignment of spectrum (*b*) in Figure 1 to the monomeric nitrosomethane, trifluoronitrosomethane was chosen as a reference compound. It is known that (*i*) CF_3NO is monomeric,[14] and (*ii*), from p.e. spectra of analogous methyl and trifluoromethyl compounds, CF_3 substituents will stabilize both σ and π m.o.s. [A nearly parallel shift of corresponding ionization potentials (i.p.s) to higher energies was found by comparing analogous pairs $CH_3R \leftrightarrow CF_3R$.[17]] The p.e. spectrum of CF_3NO [Figure 1(*c*)] shows only one band in the lower-energy region shifted by 1.2 eV to higher energies relative to (*b*). It thus confirms our statement that spectrum (*b*) in Figure 1 originates from monomeric MeNO.

Unambiguous assignment of the p.e. bands at 15—18 eV is prevented by strong overlap with n_F bands. But there is evidence that n_F m.o.s are stabilized to the same extent relative to those of CHF_3 [17,18] [Figure 1(*c*)] indicating the stronger electron-attracting power of the NO group.

Nitrosyl Halides.—To see whether experimental i.p.s could throw further light on the differing statements on the character of the highest-occupied orbital of NOF,[7,8] the p.e. spectrum of this compound was recorded together with that of NOCl [Figure 1(*d*) and (*e*)]. The spectra are assigned on the basis of CNDO (Figure 2) and EHMO calculations and qualitative considerations. The most striking feature of the spectrum of NOF is the relatively low i.p. of the fluorine lone-pair orbitals (n_F), while the n_{Cl} bands appear in their characteristic energy range (Table 2). On the other hand, π_{NO} i.p.s of NOF are observed at higher energies compared to the NO

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[15] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 1970, **53**, 684.

[16] Tae-Kyu Ha and U. P. Wild, *Chem. Phys. Letters*, 1974, **4**, 300.

[17] S. Elbel and H. tom Dieck, *Z. Naturforsch.*, 1976, **B31**, 178; A. H. Cowley, M. J. S. Dewar, and D. W. Goodman, *J. Amer. Chem. Soc.*, 1975, **97**, 3653.

[18] C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, 1970, **53**, 2196.

radical.[19] This is different from the corresponding p.e. bands of NOCl, where the π_{NO} band is found rather close to that of free NO.

TABLE 2

Comparison of n_F lone-pair orbital ionization energies (eV) of some RX compounds (X = F or Cl; R = NO, H, Me, or SiH_3)

I.e. (e.v.)	X–NO	X–H [a]	X–CH_3 [b]	X–SiH_3 [c]
n_F	14.2	16.05	17.1	16.2
n_{Cl}	11.6	12.74 12.82	11.28	11.61

[a] H. J. Lempka, T. R. Passmore, and W. C. Price, *Proc. Roy. Soc.*, 1968, **A304**, 53. [b] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, 1970. [c] S. Cradock and R. A. Whiteford, *Trans. Faraday Soc.*, 1971, **67**, 3425.

These experimental results indicate that in NOF both molecular fragments, F and NO, disturb each other noticeably in accordance with Peslak's calculations, and that F–NO bonding is not restricted to a single m.o. However, a description similar to that of Peyerimhoff and Buenker[7] derived from their NOF *ab initio* results can be applied to the NOCl molecule. Here, the larger Cl–N bond distance may reduce X–N interactions even more.

The first band of NOF exhibits vibrational fine structure with seven peaks separated by $\Delta\nu \sim 660$ cm^{-1}. This can either be associated with an enhanced ν_2 or a reduced ν_3 vibration[16,20] of the positive ion (Figure 3). *Ab initio* calculations offer little help in assigning the vibrational fine structure since, depending on the calculations, they call for F–N bonding[7] as well as for F–N antibonding.[8] Both descriptions could be used equally well to interpret the fine structure (Figure 3). However, if Peslak's calculations are accepted as those more suitable to describe the electronic structure of NOF (as indicated above), it follows that the fine structure is caused by the ν_2 vibration. High resolution of the first band of NOCl shows only small splitting with two peaks which are hardly separated.

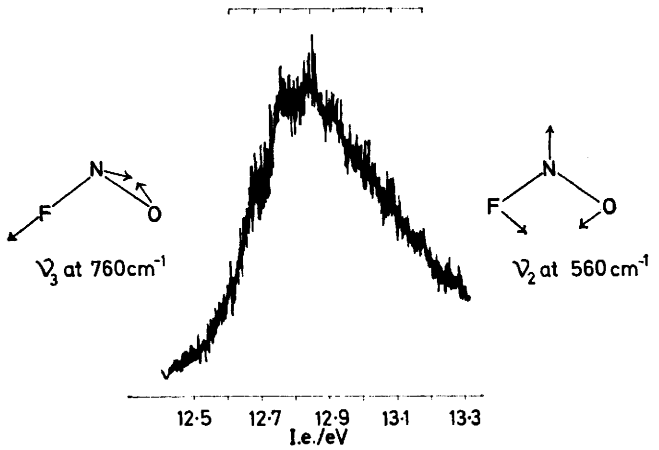

FIGURE 3 First p.e. band of NOF and the two modes of vibration which might cause the splitting

M.O. Calculations.—CNDO and EHMO calculations were carried out to support the interpretation of the p.e. spectra and to enable a comparison of the bonding in these four compounds. Our results agree satisfactorily with the p.e. energy sequence (Figure 1) and with known orbital energies of HNO,[8] MeNO,[16,21] and NOF,[8] whereas CNDO eigenvalues of HNO provided by Boyd[22] and NOF energies[7] differ appreciably.

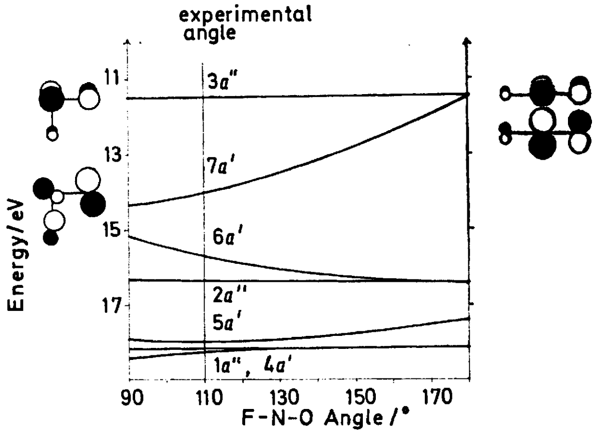

FIGURE 4 Walsh diagram of EHMO orbital energies of nitrosyl fluoride

The following points are to be stressed. The character of the highest-occupied orbital (n^- or 7*a*′), describable by strong π_{N-O} antibonding and weaker σ_{X-N} bonding contributions, remains unaltered within the series XNO (Figure 2). Varying electron densities are caused by differing X-group electronegativities. Whether bonding or antibonding X–N contributions exist in the 7*a*′ m.o.,[7–9] they can be analyzed by use of a Walsh diagram[23] (Figure 4) or by inspection of the respective coefficients of this eigenvector[21] given in Figure 2. As is shown in Figure 4 the 7*a*′ m.o. is distinctly π antibonding in its character according to the linear F–N–O configuration. By decreasing the F–N–O angle and the molecular symmetry, rather strong σ_{F-N} bonding is gained. Since 7*a*′ is much more sensitive to changes in the angle X–N–O than the other occupied *a*′ orbitals, it might indicate a predominant σ_{X-N} component. Yet, a typical σ_{X-N} orbital cannot be defined as a consequence of low molecular symmetry. The orbitals 5*a*′ and 4*a*′ also show significant σ_{X-N} contributions, as discussed by Peslak *et al.*[8] X–N antibonding contributions to X–N bonds with respect to the equilibrium angles (111—120°) cannot be confirmed by our calculations. From wavefunctions (Figure 2), stronger X–N bonding in the 7*a*′ m.o. was obtained for X = F or Cl compared to X = Me or CF_3.

The agreement between the experimental i.p.s and the sequence of CNDO energies stimulated further calculations of bond orders. CNDO bond orders were calculated by the method of Boyd[24] and are compared with

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[19] O. Edqvist, L. Åsbrink, and E. Lindholm, *Z. Naturforsch.*, 1971, **A26**, 1407.

[20] P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, *J. Chem. Phys.*, 1952, **20**, 378.

[21] J. Kuhn, W. Hug, R. Geiger, and G. Wagnière, *Helv. Chim. Acta*, 1971, **54**, 2260.

[22] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. (A)*, 1971, 3579.

[23] A. D. Walsh, *J. Chem. Soc.*, 1953, 2296.

[24] R. J. Boyd, *Canad. J. Chem.*, 1973, **51**, 1151.

TABLE 3

Comparison of calculated bond orders and dipole moments of NO and XNO molecules (X = H, F, Cl, Me, or CF_3) with experimental data

	CNDO bond orders and atomic charges					EHMO reduced Mulliken overlap populations and atomic charges					Experimental stretching force constants (f/mdyn cm^{-1})[a] and bond orders (n)		Calculated (and *experimental*) dipole moments (μ/D)[b]
NO			+0.10 N	σ 1.00 π 1.40 Σ 2.40	−0.10 O						f(N–O) n(N–O) n(N–O)	15.5 (ref. 9) 2.06 (ref. 6) 2.5 (ref. 11)	0.19[c] (0.16)[d]
HNO	+0.10 H		+0.06 N	σ 0.98 π 1.05 Σ 2.03	−0.16 O	+0.30 H	0.67	−0.02 N	0.93	−2.28 O	f(N–O) n(N–O)	10.5 (ref. 9) 2.0 (ref. 11)	2.25[c]
NOF	−0.27 F	σ 0.91 π 0.13 Σ 1.04	+0.36 N	σ 0.98 π 1.39 Σ 2.37	−0.09 O	−0.66 F	0.17	+0.69 N	1.28	−0.03 O	f(N–O) n(N–O) f(F–N) n(F–N)	14.67 (ref. 9) 1.98 (ref. 6) 2.3 (ref. 6) 0.5 (ref. 6)	1.33[c] 0.73 (ref. 7) 0.33 (ref. 10) (1.81) (ref. 7)
NOCl	−0.23 Cl	σ 0.89 π 0.09 Σ 0.98	+0.30 N	σ 0.99 π 1.39 Σ 2.38	−0.07 O	−0.17 Cl	0.38	+0.34 N	1.14	−0.17 O	f(N–O) n(N–O) n(N–O) f(N–Cl) n(N–Cl)	14.1 (ref. 9) 1.92 (ref. 6) 2.5 (ref. 11) 2.0 (ref. 6) 0.5 (ref. 6)	2.10 (−d)[c] 0.87 (+d)[c] 1.83 (ref. 25)
MeNO	0.0 C	σ 0.95 π 0.19 Σ 1.14	+0.11 N	σ 1.03 π 1.03 Σ 2.01	−0.21 O	+0.26 C	0.70	+0.02 N	0.90	−0.42 O			2.62[c] 1.53 (3.50), (ref. 21)
CF_3NO	+0.79 C F −0.25	σ 0.93 π 0.17 Σ 1.10	+0.06 N	σ 0.97 π 1.10 Σ 2.07	−0.11 O	+2.25 C F −0.64	0.64	−0.05 N	0.95	−0.26 O	f(N–O)	10.1[e]	0.07[c] 1.5—1.9 predicted (0.31)[f]

[a] 1 dyn = 10^{-5} N. [b] 1 D ≈ 3.33 × 10^{-30} C m. [c] Our own CNDO calculations modified according to ref. 13 with *d* orbitals included (+ d) or excluded (− d). [d] C. A. Burrus and J. D. Graybeal, *Phys. Rev.*, 1958, **109**, 1553. [e] H. F. Shurvell, S. C. Dass, and R. D. Gordon, *Canad. J. Chem.*, 1974, **52**, 3149. [f] J. E. Boggs, D. Coffey, J. C. Davis, D. J. Millen, and J. Pannell, *J. Chem. Soc.*, 1961, 1322.

EHMO (reduced Mulliken overlap populations) and experimental bond orders in Table 3. The CNDO data show slightly increased N–O bond orders in NOX (X = halide) molecules probably due to larger ionic contributions, and similar X–N bond orders in all XNO molecules discussed here. EHMO overlap populations seem to reproduce better experimental f(N–X) stretching force constants, but are generally too small. Furthermore, charges on the atoms are exaggerated by the EHMO theory. The relative positions of the higher i.p.s (Figure 1) are well understood by a hyperconjugative m.o. model, if inductive perturbation is included. This concept seems to be reasonable, for a strong electron-withdrawing effect was found for the NO group.[25]

In *C*-nitroso-compounds the X units are positively charged, whereas a reversal of this charge distribution occurs in nitrosyl halides (*cf.* Table 3). This change is accompanied by an opposite shift (±*I*) of the relative X and NO energy levels. The different splitting pattern thus obtained is displayed in Figure 5, exemplified by the relative experimental energies of the π-type orbitals of the parent molecules [*e.g.* NO,[19] HX (see Table 2), and CH_4 [18]]. In the NOX (X = halide) molecules the n_X orbitals are shifted to lower energies and consequently destabilized further by hyperconjugation (*H*). In MeNO it is the *a''* NO orbital which is lowered in his manner.

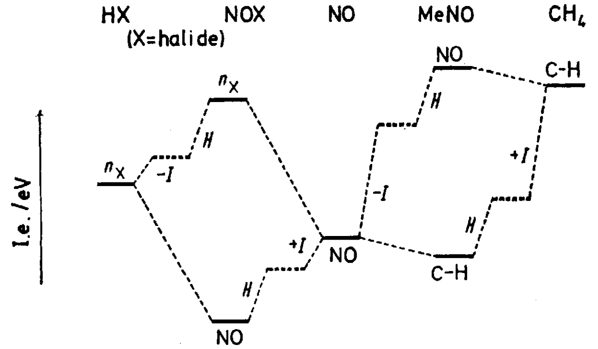

FIGURE 5 Qualitative ' composite-molecule ' model showing the inductive (*I*) and hyperconjugative (*H*) interactions between X and NO units of XNO molecules (X = halide or Me) according to the relative experimental π reference levels of NO and HX

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[25] M. Tanaka, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1966, **39**, 766.

APPENDIX

After submission of this paper a report on nitrosyl and nitryl halides and nitric acid was published by Frost *et al.*[26] The p.e. spectra of NOF and NOCl, discussed in both papers, were assigned in the same manner to the different molecular orbitals. Also, in the spectrum of NOF equal separation of the first and second band was found (1.56 and 1.54 eV, respectively), but there is a discrepancy of 0.2 eV between our (absolute) values for the first and the second ionization potentials and those of Frost *et al.* As our spectrum was calibrated by the decomposition products NO and HF, which embrace the two NOF bands in question, we are confident of our i.p. values. However, further investigations would seem to be appropriate to clarify matters.

In a recent publication Egdell *et al.*[27] presented He(I) spectra of several *C*-nitroso-compounds. Their spectrum of nitrosomethane differs substantially from our spectrum discussed here and earlier in a short note.[28] During our investigations we obtained the same spectra of *trans*-nitrosomethane and *trans*-1,1-dimethyl-1-nitrosoethane as Egdell *et al.*, but we assign them to the dimeric species. In order to help clarify this basic discrepancy, we present below some arguments supporting our interpretation.

Figure 1 shows that at elevated temperatures a simple p.e. spectrum evolves from that of dimeric *cis*-nitrosomethane, indicating the formation of smaller molecules from a more complicated one. From unpublished results on hydroxylamines and -imines,[13] we conclude that the smaller molecule could not be formaldehyde oxime, but should be monomeric nitrosomethane.

For comparison the p.e. spectra of other nitroso-compounds were recorded (Figure 1 shows some of them). The spectra of the relatively simple molecules CF_3NO and NOF, both certainly monomeric in the gas phase, clearly demonstrate that our spectrum assigned to monomeric MeNO matches this group well, whereas Egdell's spectrum shows a band pattern in the low-energy region which is not compatible with our reference spectra.

From the π i.p.s of the isoelectronic molecules $MeCH{=}CH_2$ (9.7 eV)[29] and MeCH=O (13.24 eV)[30] one expects the corresponding π band of MeN=O at or above 14 eV. This is fulfilled in our spectrum, whereas Egdell *et al.* reported a value of 10.93 eV.

Several independent m.o. calculations on HNO and monomeric and dimeric nitrosomethane qualitatively support our assignment above. In the case of HNO[31] and MeNO[16] there is a relatively large energy gap between the levels of the n^- m.o. on the one hand and the n^+ and π(NO) orbitals on the other, the energy levels of the latter m.o.s being close together. Even after corrections to Koopmans' theorem this pattern is clearly preserved.[31] However, looking at the calculations of dimeric nitrosomethane[21] one finds a similarity between the spacing of energy levels in the low-energy region and the band pattern in the p.e. spectrum of MeNO of Egdell *et al.*

There remain some minor questions raised by the results of Egdell *et al.* (*a*) In mass-spectrometric studies of *trans*-$(MeNO)_2$ they find ' a significant portion of dimer in the vapour phase ', but did not stress this important fact in their discussion. (*b*) As the 1*s* and 2*s* electrons of C, N, and O appear at higher energies, an He(I) spectrum of monomeric MeNO should exhibit not more than six bands. However, in Egdell's spectrum at least seven (up to nine) bands can be distinguished. This may indicate that those workers probably observed a molecule larger than monomeric nitrosomethane. (*c*) Compared to the i.p.s of π(NO) of the NO radical (>16 eV)[32] or of NOF (>18 eV),[26] the corresponding value of Egdell *et al.* for MeNO (10.93 eV) seems to be unusually low. No m.o. calculation known to us indicates a destabilizing effect causing such a tremendous shift in the i.p.s of π(NO).

The spectra of Egdell *et al.* for the certainly dimeric carboxyl derivatives, although being too complicated to give any unambiguous interpretation, seem to match fairly well their own spectra of nitrosomethane and 1,1-dimethyl-1-nitrosoethane. If this observation turns out to be correct, it can be considered an intrinsic proof of the correctness of our assignment.

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