

A SEMIEMPIRICAL MOLECULAR ORBITAL STUDY OF RADICALS AND RADICAL IONS DERIVED FROM CARBON OXIDES

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Semiempirical CNDO-CI calculations were performed for radical anions $\text{CO}^{\dot{-}}$, $\text{CO}_2^{\dot{-}}$ and $\text{CO}_3^{\dot{-}}$, their protonated forms and the hydrated form of $\text{CO}^{\dot{-}}$. Optimized geometries were employed. With $\text{CO}^{\dot{-}}$ and $\text{CO}_2^{\dot{-}}$, the calculations represent further progress in the interpretation of electronic spectra. It seems that the absorption curve assigned to $\text{CO}_2^{\dot{-}}$ by experimentalists is due to the *trans*- OCOH^{\bullet} species. The calculations do not support the assignment of the band observed at $17\,000\text{ cm}^{-1}$ to $\text{CO}_3^{\dot{-}}$ or $\text{CO}_3\text{H}^{\bullet}$.

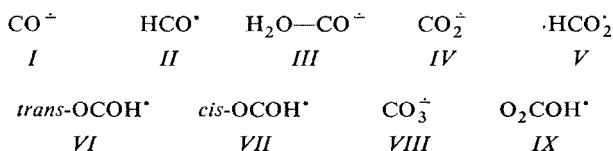
Recently, it has been established^{1,2} that the open shell version of the CNDO/S method of Del Bene and Jaffé³ gives a good interpretation of the electronic spectra of open shell systems. This applies to radicals having nondegenerate ground states. In treatments of radicals and radical ions having degenerate ground states^{4,5}, the INDO level of approximation must be used, otherwise the splitting of some excited electronic states owing to one-centre exchange interactions is not accounted for⁶. The stimulus for the present study arose from the circumstance that the electronic spectra of radicals and radical ions provided by the pulse radiolysis and photolysis techniques are considered somewhat inferior compared to spectra given by other methods. This is understandable because the unstable, extremely reactive species react instantaneously with other products of radiolysis and photolysis after a generating pulse. Sometimes it is uncertain whether the rapid spectrophotometer is scanning the spectrum of anticipated species, their hydrated or protonated forms, or a spectrum of a product of their decomposition. In our opinion, pulse techniques still represent an extremely valuable source of information about the spectra of short-lived species. But in interpreting the observed spectra a large use of theoretical data should be made. Here it is more topical than in other fields.

The subject of the present paper is a theoretical study of radicals and radical anions derived from carbon oxides. Its prime aim is the comparison of calculated spectral characteristics with the observed spectra of species generated in solution by the pulse radiolysis technique. Furthermore, relative stabilities of isomers are discussed⁷ on the basis of the computed total energies. Since the systems studied are extremely reactive, we also examined their protonated and hydrated forms.

Systems Studied and Calculations

The systems studied *I*–*IX* comprise radical anions of CO (*I*), CO_2 (*IV*) and CO_3 (*VIII*). The others among *I*–*IX* may be considered to originate from *I*, *IV*, and *VIII* by protonation (*II*, *V*,

VI, VII, IX) and hydration (*III*).



Optimized geometries were used throughout the calculations. The automatic minimization procedure⁷ was based on the CNDO/2 method⁸. Use has been made of the open shell procedure of Longuet-Higgins and Pople⁹. Total energies were computed by CNDO/2, and for selected systems also by MINDO/2 (ref.¹⁰). Transition energies, ionization potentials, electron affinities, charges, dipole moments and spin densities were calculated by the CNDO/S method³ and its modified version^{4,6} on the INDO level (hereafter referred to as INDO/S). The LCI calculations were performed in the virtual orbital approximation as described in our earlier papers^{1,4}.

RESULTS AND DISCUSSION

Geometries. Optimized CNDO/2 geometries of systems *I, II, IV–IX* are presented in Fig. 1. Minimization was performed with the restriction that all systems are planar. This conforms to the assumption reported in ref.¹¹. Agreement with experiment¹² for *II* is fair (compare ref.¹), but the calculated bond angle is overestimated by 8°. Also with *IV* the predicted angle is 4° greater than the observed angle¹³; compared to the observed bond length¹⁴ the predicted bond length is longer by 0.08 Å. Among the isomers of protonated CO_2^- (*V–VII*), the structure *VI* and *VII* protonated on oxygen appear to be more stable than *V*. Geometry optimization of *VIII* deserves a special comment. On starting it with the C_{3v} symmetry, the HOMO becomes nondegenerate which brings about a decrease in energy (Jahn–Teller effect). The optimal bond angle of 68° suggests a rather close attachment of a pair of O atoms. The same geometry (compare Fig. 1) resulted from the minimization which started from the structure with the 170° bond angle. Hence theory predicts a structure of the C_{2v} symmetry (see also ref.¹¹). Experimentally^{14,15} (see also papers cited in ref.¹¹) both C_{2v} and D_{3h} structures are suggested. The data for the latter are 1.303 Å for the C–O bond length¹⁴ and 120° for the bond angle¹⁵. Fig. 1 also presents the calculated charge and spin densities. We used them in considerations about the possible protonation sites.

Ionization potentials, electron affinities, total energies, and dipole moments. These are entered in Table I. The ionization potentials are of course very low for anions. The CNDO/S results differ from the INDO/S results by about 0.5 eV. The ionization potential for *I* (degenerate ground state) was calculated in two ways. Firstly, it was taken to be the difference between the total energies of CO^- and CO .

Secondly, assumptions involved in the Koopmans theorem were applied. In this special case the following expression results

$$-I^m = \varepsilon^m - \frac{1}{4} J^{mm} - \frac{1}{2} J^{mn} + \frac{1}{4} K^{mn} \quad (1)$$

where ε is orbital energy given by our open shell approach, m and n are indices for a pair of MOs constituting the open shell and the other symbols have their usual meaning.

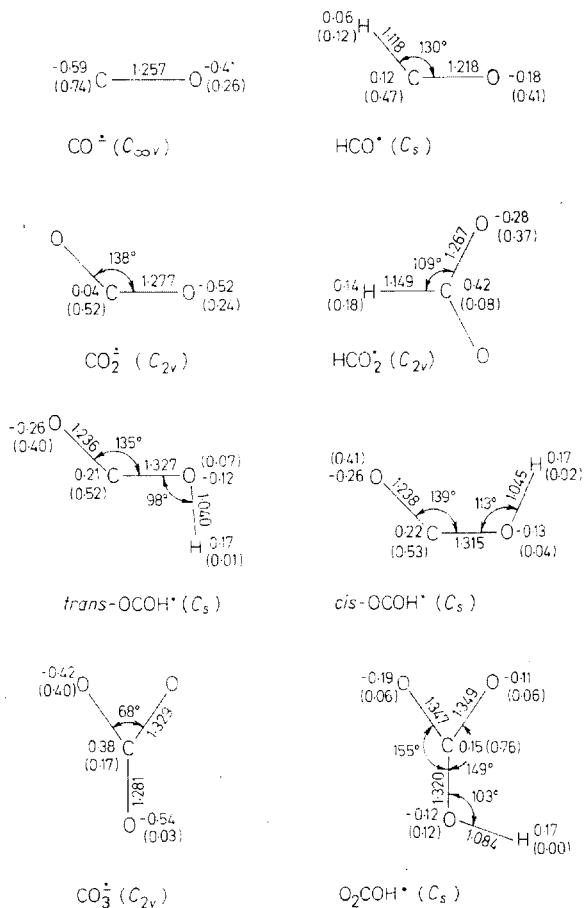


FIG. 1
Equilibrium Geometries, Charges and Spin Densities (in parentheses)
Bond length in Å.

Total CNDO/2 energies for isomers of protonated CO_2^+ (systems *V–VII*) differ rather little. A more useful result is provided by MINDO/2 which favours unambiguously the O-protonation over the C-protonation; the *trans* isomer should be by 10 kcal/mol more stable than the *cis* isomer (Table I). This conforms to what is expected about the isomers if the estimates of their structure are based on electron and spin densities distribution in *IV*.

Electronic spectra. Theoretical spectral characteristics for the doublet-doublet transitions in *I–IX* are entered in Table II. Since with radicals having degenerate ground states the INDO level of approximation is superior to the CNDO level⁶, we also performed the INDO/S calculation for *I*. To make sure that the two methods give consistent predictions of band locations for radicals with nondegenerate ground states, the INDO/S calculations for *IV* and *VIII* were performed, too.

A band assigned to the radical anion *I* was observed¹⁶ at 38460 cm^{-1} ($\log f = -1.42$). INDO/S predicts that the lowest energy transition is a ${}^2A \leftarrow X^2\Pi$ transition followed by ${}^2\Sigma^+ \leftarrow X^2\Pi$ and ${}^2\Sigma^- \leftarrow X^2\Pi$; due to the neglect of one-center exchange interactions, CNDO/S gives a single value for the three transition energies. Agreement between theory and experiment is good, nevertheless the presence of the protonated form *II* cannot be ruled out (compare data in Table II and the observed spectrum of the formyl radical¹⁷). In order to confirm the assignment to *I*, it would

TABLE I
Ground State Characteristics^a

I, *A* ionization potential and electron affinity, *E* total energy, μ dipole moment in Debye.

System	<i>I</i>	<i>A</i>	<i>E</i> (CNDO/2)	<i>E</i> (MINDO/2)	μ
CO^+	0.34 ^{b,c}	0.22 ^{b,d}	—	—	—
	1.03 ^c	0.37 ^d	—	—	—
HCO^+	9.87	1.62	—	—	2.04
$\text{H}_2\text{O}-\text{CO}^+$	0.61	-8.61	—	—	—
CO_2^+	2.61	-5.27	-1185.00	—	—
	2.14 ^b	-6.60 ^b	—	—	—
HCO_2^+	11.19	3.83	-1207.72	-767.43	2.85
<i>trans</i> - OCOH^+	9.70	1.37	-1207.63	-769.64	3.32
<i>cis</i> - OCOH^+	9.79	1.35	-1207.73	-769.25	2.78
CO_3^+	1.32	-7.06	-1689.99	—	—
	0.72 ^b	-8.07 ^b	—	—	—
O_2COH^+	8.51	-0.51	-1715.26	—	2.72

^a CNDO/S data in eV unless otherwise stated; ^b INDO/S data; ^c calculated from Eq. (1); ^d calculated from $-I = E(\text{CO}^+) - E(\text{CO})$.

be necessary to establish that the spectrum is free of any absorption in the region at 12000 cm^{-1} under the given experimental conditions. Theory does not support the assignment of the observed band to the hydrated form. It predicts two bands for that system: one band at $44\,250\text{ cm}^{-1}$ and, remarkably enough, one band in the infrared region (at 1240 cm^{-1}). The latter is of a charge-transfer nature and originates in a $\pi \rightarrow \sigma^*$ type transition. Finally, it should be noted that theory gives¹ a good account of the gas-phase spectrum of the formyl radical (II).

A weak absorption band observed at 27400 and 29400 cm^{-1} in solid matrices (γ -irradiation of sodium formate) was assigned to the radical anion IV (ref.^{18,19}). There is a good agreement between the second (forbidden; at 28360 cm^{-1}) and the third (allowed) CNDO/S transitions (at 28680 cm^{-1}) and the observed values.

TABLE II
Electronic Spectra

System	$\tilde{\nu}^a$	$\log f^b$	System	$\tilde{\nu}^a$	$\log f^b$		
CO ⁺	CNDO/S	46.80	-1.7694	HCO ₂ ⁻	CNDO/S	5.39	-1.8256
	INDO/S	41.65	-1.5528		5.57 ^c	—	
		47.68	-1.8239		26.63 ^c	—	
		49.63	-1.4948		31.92	-5.7843	
CO ₂ ⁺	CNDO/S	11.69	-2.7070	40.51 ^c	—		
		28.36 ^c	—	45.96	-5.1454		
		28.68	-1.6709	46.95	-2.4535		
		42.21 ^c	—	CO ₃ ⁺	CNDO/S	27.55 ^c	—
		47.62 ^c	—		39.88 ^c	—	
	INDO/S	12.62	-2.6391		54.27	-0.8596	
		34.76	-2.0336	INDO/S	25.00 ^c	—	
	37.06 ^c	—	44.42 ^c	—			
	43.36 ^c	—	51.65	-1.2720			
	47.25	-2.3940	H ₂ O—CO ⁺	CNDO/S	1.24	-5.7507	
<i>cis</i> -OCO ⁺ H	CNDO/S	14.38	-2.4719	44.25	-1.6336		
		29.72	-2.9060	45.61 ^c	—		
		34.46	-1.5036	<i>trans</i> -OCO ⁺ H	CNDO/S	14.38	-2.5370
		47.20	-2.0661		29.90	-2.9788	
HCO [•]	CNDO/S	12.23	-2.5417	34.63	-1.5332		
		36.01	-2.7025	48.71	-2.4951		
		37.26	-1.5290	O ₂ CO [•] H	CNDO/S	44.84	-3.0789
		47.31	-1.9238		48.19	-1.8661	
			59.18		-1.1345		
				59.61	-3.7268		

^a Wavenumber in 10^{-3} cm^{-1} ; ^b oscillator strength; ^c forbidden transition.

One can conclude that the first CNDO/S transition lies in the region where experimental measurement has not yet been performed. Theory predicts the following three lowest-energy transitions: ${}^2B_1 \leftarrow {}^2A_1$, ${}^2A_2 \leftarrow {}^2A_1$, and ${}^2B_2 \leftarrow {}^2A_1$. The experimentally observed transition was tentatively assigned to the ${}^2B_1 \leftarrow {}^2A_1$ transition which conforms to the only calculated²⁰ SCF *ab initio* transition. We are unable at present to analyse this discrepancy. In the paper cited a remark was made on qualitatively different conclusions resulting from semiempirical and *ab initio* calculations. We feel that the available *ab initio* excitation energy is of limited use for our discussion for several reasons: 1) the transition energy was derived from the total energy as a function of bonding angle. However the CO bond length was fixed at 2.196 au which is the equilibrium CO distance in the neutral CO₂, 2) the transition moment was not calculated, 3) for a valuable discussion three longest-wavelength *ab initio* transitions would be necessary.

Fig. 2 presents the absorption curve assigned to the radical anion CO₂⁻ (IV) in the aqueous solution and the results of calculations for IV and its protonated forms V, VI, and VII. Since the absorption curve²¹ was recorded only in the region 29000 to 45000 cm⁻¹, it is difficult to say whether theory supports the assumed assignment. It is only possible to state that the theoretical data for the two O-protonated forms (VI, VII) match the absorption curve. However the entries of Table II and Fig. 2 suggest that the absorption curve is measured incompletely and that the next band can safely be expected to lie in the region of 14000 cm⁻¹ (with V in the region of

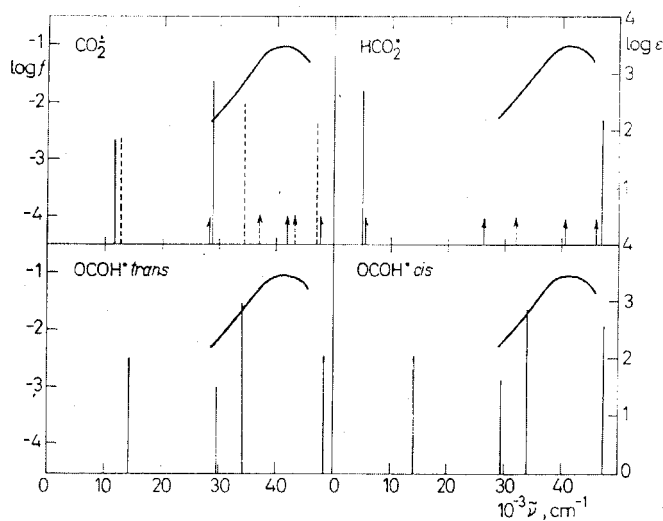


FIG. 2
Predicted Electronic Transitions in CO₂⁻ and Its Protonated Forms

In all four cases a comparison is made with the observed absorption curve¹⁸ assigned to CO₂⁻. Calculated transitions are denoted by solid (CNDO/S) and dashed (INDO/S) vertical lines, arrows indicate forbidden transitions.

5000 cm^{-1}). Hence, also here theory gives useful suggestions for the experimental work. It has been supposed²¹ that *IV* and its protonated form have almost identical spectra. The results of calculations are roughly consistent with that supposition but only as far as the first two allowed transitions are involved. A theoretical study of hydrated forms of *IV* will become topical at the moment when more complete spectral data will be available.

With the radical anion *VIII* and its protonated form *IX* the theory does not give a satisfactory interpretation of experiment. Up to now, the absorption curve available²²⁻²⁴ covers only a narrow region of 14000–25000 cm^{-1} . It exhibits one band with the maximum at 17000 cm^{-1} . Theory disagrees with experiment to such an extent that the assignment of the observed band to *VIII* should be taken with caution. Further progress in the solution of this problem requires augmentation of the experimental data and calculations for additional model systems derived from the radical anion *VIII*.

REFERENCES

1. Zahradník R., Čársky P.: *Theoret. Chim. Acta* 27, 121 (1972).
2. Čársky P., Macháček M., Zahradník R.: *This Journal* 38, 3067 (1973).
3. Del Bene J., Jaffé H. H.: *J. Chem. Phys.* 48, 1807 (1968).
4. Kuhn J., Čársky P., Zahradník R.: *Theoret. Chim. Acta* 33, 263 (1974).
5. Kuhn J., Čársky P., Zahradník R.: *This Journal* 39, 2175 (1974).
6. Čársky P., Kuhn J., Zahradník R.: *J. Mol. Spectry* 55, 120 (1975).
7. Pancíř J.: *Theoret. Chim. Acta* 29, 21 (1973).
8. Segal G. A.: *J. Chem. Phys.* 47, 1876 (1967).
9. Longuet-Higgins H. C., Pople J. A.: *Proc. Phys. Soc. (London)* 68A, 591 (1955).
10. Dewar M. J. S., Haselbach E.: *J. Am. Chem. Soc.* 92, 590 (1970).
11. Olsen J. F., Burnelle L.: *J. Am. Chem. Soc.* 92, 3659 (1970).
12. Pedersen L.: *J. Mol. Structure* 5, 21 (1970).
13. Ovenall D. W., Whiffen D. H.: *Mol. Phys.* 4, 135 (1961).
14. *Tables of Interatomic Distances and Configuration in Molecules and Ions*. The Chemical Society, London 1965.
15. Elliott N.: *J. Am. Chem. Soc.* 59, 1380 (1937).
16. Fojtík A., Czapski G., Henglein A.: *J. Phys. Chem.* 74, 3204 (1970).
17. Herzberg G.: *Molecular Spectra and Molecular Structure*. III. Nostrand, Reinhold Comp., New York 1969.
18. Hartman K. O., Hisatsune I. C.: *J. Chem. Phys.* 44, 1913 (1966).
19. Chantry G. W., Whiffen D. H.: *Mol. Phys.* 5, 189 (1962).
20. Krauss M., Neumann D.: *Chem. Phys. Letters* 14, 26 (1972).
21. Neta P., Simic M., Hayon E.: *J. Phys. Chem.* 73, 4207 (1969).
22. Weeks J. L., Rabani J.: *J. Phys. Chem.* 70, 2100 (1966).
23. Hayon E., McGarvey J. J.: *J. Phys. Chem.* 71, 1472 (1967).
24. Behar D., Czapski G., Duchovny I.: *J. Phys. Chem.* 74, 2206 (1970).

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