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Theoretical Study of the Electronic Spectrum of Carbonyl Cyanide

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The ground state properties of carbonyl cyanide and the energies of the electronic transitions are determined by means of the CNDO/2 and CNDO/CI methods respectively. The calculated results are correlated with the observed electronic spectra and assignments are suggested for some previously unassigned transitions. The bonding and delocalization of the π electrons of the ground and excited states of the molecule are discussed through an analysis of the molecular orbitals and charge density distributions.

Die Eigenschaften des Grundzustandes von Carbonylcyanide und die Energie von elektronischen Übergängen werden mit Hilfe der Methoden CNDO/2 und CNDO/CI bestimmt. Die berechneten Ergebnisse werden mit dem beobachteten Elektronenspektrum korreliert; für einige bisher nicht klassifizierte Übergänge werden Zuordnungen vorgeschlagen. Die Bindung und Delokalisierung der π-Elektronen des Grundzustandes und der angeregten Zustände werden mit Hilfe einer Analyse der MO's und der Ladungsverteilung diskutiert.

Introduction

The absorption spectrum of carbonyl cyanide, $(CN)_2CO$, has been the subject of a number of recent investigations. The spectrum was first studied by Kemula and Wierzchowski [1] and more recently by Wierzchowski *et al.* [2] who examined the absorption and fluorescence spectrum of the $n \rightarrow \pi^*(^1A_2 \leftarrow \tilde{X}\,^1A_2)$ transition at high and intermediate dispersion. The spectrum in the vacuum ultraviolet region has just been reported by Duncan and Whittock [3]. Only one resolved transition was observed between 46900 and 78100 cm^{-1}. Since their experimental data was not sufficient to make an assignment for the above transition, we decided that a theoretical treatment might aid the interpretation of the electronic spectrum. As far as we can ascertain, no detailed theoretical study has been previously carried out for carbonyl cyanide. The two cyanogen groups attached symmetrically to a carbonyl group should provide an interesting study of the mixing of the π orbitals of the CO and CN groups as well as the mixing of the n orbitals of the atoms.

In this paper, we report the application of the CNDO method [4–7] to the study of the ground state and electronic spectrum of carbonyl cyanide. This method should be quite suitable since it treats all valence electrons.

Table 1. Bond distance and angles used for carbonyl cyanide

Bond	Distance, Å	Angle	Size, deg
C=O	1.220[a]	C–C–C	115° 19
C≡N	1.165[a]	C–C–N[a]	0
C–C	1.450		

[a] Assumed.

Method of Calculation

For the calculation of the ground state properties of carbonyl cyanide, the CNDO/2 method [6] was adopted without modification. The parameters used were those developed by Pople and Segal [5, 6]. In this form, the method has been successfully applied to ground state calculations of many small molecules.

Since the CNDO/2 method gives very poor results when applied to the treatment of excited state properties, the electronic spectrum of carbonyl cyanide was computed using the modification of the CNDO/2 method proposed by Del Bene and Jaffé [8]. This method has been satisfactorily applied in the prediction of both $\pi \rightarrow \pi^*$ and $n - \pi^*$ transitions. The parameters β_A^0 used in the program to estimate the resonance integrals between carbon, oxygen and nitrogen were taken to be the same as those suggested by Jaffé [8]. In the Jaffé modification, the two-centre Coulomb integrals were evaluated by the extrapolation technique proposed by Pariser [9]. However, in our calculations, we have used a modified Mataga-Nishomoto approximation [10] for these integrals since we feel that this method leads to slightly better results [11].

The bond distances and angles of carbonyl cyanide chosen for the calculations are given in Table 1. These values were obtained from a recent analysis of the microwave spectrum by Lees [12]. In their determination of the molecular parameters, they assumed that the CCN chain was linear. Since their data were consistent with a planar structure, we assumed in our work that carbonyl cyanide was planar with C_{2v} symmetry. By convention [13], we have chosen the C_2 axis as the z-axis and the x-axis as perpendicular to the molecular plane.

Results of the Calculations

a) Ground State Properties

The ground state properties of carbonyl cyanide were obtained by the original CNDO/2 method and also by the Jaffé modification. The charge density distributions on the nuclei are given in Fig. 1. These represent the flow of charge in the molecule from the neutral atoms. One can see that the Jaffé method leads to a greater total net charge on the nuclei. Both schemes lead to a polarization of the π electrons (formed from the $2p_x$ orbitals of the nuclei) on the carbonyl group. The π bond can be designated $C^+ - O^-$ and is quite polar in contrast to the analogous bond in formaldehyde. The π electrons of the remaining nuclei are polarized only slightly.

Berthier, Pullman, and Pontis [14] have found that the characteristic carbonyl stretching frequency of aldehydes and ketones gives an excellent

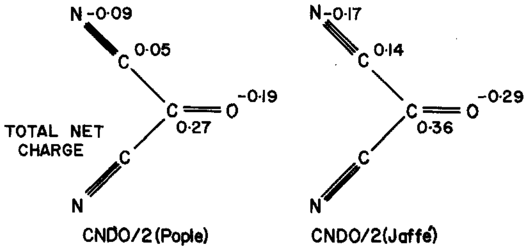

Fig. 1. Charge density distributions for the $\tilde{X}\,^1A_1$ ground state of carbonyl cyanide as calculated by a) CNDO/2 (Pople) and b) CNDO/2 (Jaffé)

correlation with the π-bond order of the carbonyl group. In order to assess our calculations, we have determined the carbonyl frequency with this correlation using our values of 0.913 (CNDO/2) and 0.914 (Jaffé) for the π-bond order between carbon and oxygen. We obtained 1710 and 1711 cm^{-1} respectively. Experimentally the carbonyl frequency is observed at 1712 cm^{-1} [15].

Our results also show that the oxygen $2p_y$ orbital (the n-orbital) is not completely full. There is a "back-donation" effect present in which electrons in orbitals of this symmetry (b_2) are transferred into the antisymmetric $C(CN)_2$-orbitals forming a partial pseudo-π bond or π_y bond. Similarly as with formaldehyde, there is a concentration of oxygen lone pair electrons on the z-axis on the side away from the rest of the molecule.

The bond order defined as

$$P_{\mu\nu} = 2 \sum_{i=1}^{\text{occ}} C_{i\mu} C_{i\nu}$$

where the sum is over all the occupied orbitals and $C_{i\mu}$ are the coefficients of the LCAO SCF molecular orbitals gives a measure of the bonding due to contributions by the atomic orbitals i and j. The out-of-plane π bond orders were determined to be 0.96, 0.27 and 0.91 between nitrogen and carbon; carbon and carbon; and carbon and oxygen respectively. There is some delocalization of the π-electrons into the CCC skeleton but it is not extensive. One can regard the C–C bond as essentially a single bond. This is also demonstrated by a comparison of the "bond indices" which appear to be closely related to the bond character [16]. This quantity is given by the sum of the squares of the bond orders to an atom and corresponds to the number of covalent bonds formed by that atom, corrected for the ionic character in each bond. The bond indices determined were 2.88, 1.02 and 1.84 for $C\equiv N$, C–C, and $C=O$ respectively. Since these will be later compared with the values obtained for the first excited state, we have reported only the results for the Jaffé calculation. In any case, the values obtained by the CNDO/2 method are quite similar. The value 1.02 shows that delocalization across the CCC skeleton is small and there does not appear to be a great loss in the triple bond character of $C\equiv N$. This loss and subsequent delocalization was predicted to occur in carbonyl cyanide by Bates [15] who analysed the vibrational frequencies of a number of compounds containing the carbonyl and nitrile groups.

Both methods yield a dipole moment [0.12 D and 0.14 D (Jaffé)] which is much smaller than the experimental value of 0.70 D [12]. The energies of the

Table 2. Energies and classification of the molecular orbitals of carbonyl cyanide

Symmetry	Energy (a.u.)	Symmetry	Energy (a.u.)
$8a_1$	-0.69519	$3b_1$	-0.04237
$1b_1$	-0.63299	$11a_1$	0.02049
$5b_2$	-0.59823	$2a_2$	0.03566
$9a_1$	-0.58883	$8b_2$	0.05076
$10a_1$	-0.51399	$4b_1$	0.08000
$1a_2$	-0.50916	$12a_1$	0.11889
$6b_2$	-0.49199		
$2b_1$	-0.48688		
$7b_2$	-0.44392		

molecular orbitals as calculated by the Jaffé version of the CNDO/2 method and their group theoretical classification are given in Table 2.

b) Excited State Properties and Spectra

The electronic spectrum of carbonyl cyanide was calculated with and without the inclusion of configuration interaction (C.I.). When it was included, thirty singly excited configurations were employed. These comprised all the configurations arising from the promotion of an electron from the occupied orbitals $10a_1 - 5b_2$ to the unoccupied orbitals $3b_1 - 12a_1$ inclusive. The results of the calculations when C.I. was included are given in Table 3. The correlation with the experimental results is displayed in Fig. 2.

Table 3. Calculated electronic transitions in carbonyl cyanide

Transition	Vertical transition energy (cm^{-1})	Oscillator strength	Configuration mixing
$\tilde{A}\,{}^1A_2 - \tilde{X}\,{}^1A_1$ $(n \rightarrow \pi^*)$	24168	0	$7b_2 \rightarrow 3b_1$ (91%) $7b_2 \rightarrow 4b_1$ (8%) $6b_2 \rightarrow 3b_1$ (1%)
${}^1A_2 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	39434	0	$6b_2 \rightarrow 3b_1$ (62%) $10a_1 \rightarrow 2a_2$ (26%)
${}^1B_1 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	40777	10^{-4}	$10a_1 \rightarrow 3b_1$ (50%) $6b_2 \rightarrow 2a_2$ (41%)
${}^1B_2 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	43578	0.006	$1a_2 \rightarrow 3b_1$ (31%) $4b_2 \rightarrow 7a_1$ (30%) $2b_1 \rightarrow 7a_1$ (18%) $10a_1 \rightarrow 8b_2$ (15%)
${}^1A_1 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	44040	0.05	$2b_1 \rightarrow 3b_1$ (34%) $10a_1 \rightarrow 11a_1$ (22%) $6b_2 \rightarrow 8b_2$ (20%) $1a_2 \rightarrow 2a_2$ (19%)
${}^1A_2 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	47023	0	$1a_2 \rightarrow 11a_1$ (60%) $2b_1 \rightarrow 8b_2$ (40%)
${}^1B_1 - \tilde{X}\,{}^1A_1$ $(\pi \rightarrow \pi^*)$	47034	0	$2b_1 \rightarrow 11a_1$ (60%) $1a_2 \rightarrow 8b_2$ (40%)
${}^1B_2 - \tilde{X}\,{}^1A_1$ $(n \rightarrow \pi^*)$	54780	0.008	$7b_2 \rightarrow 11a_1$ (99%)

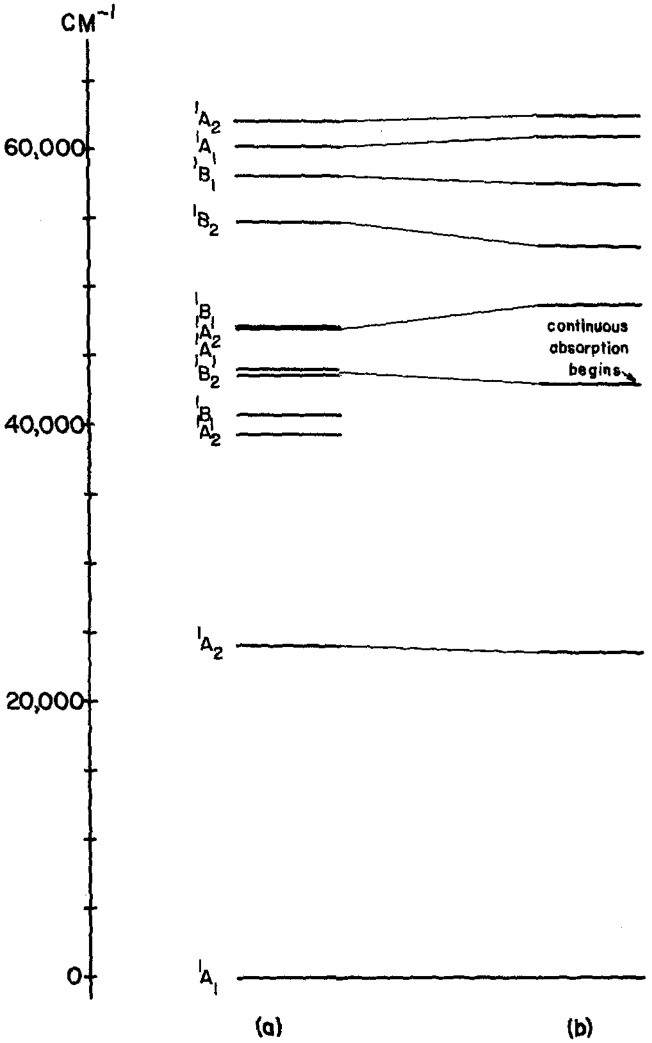

Fig. 2. Electronic states of carbonyl cyanide a calculated results with C.I. and b experimental results

The lowest electronic transition was calculated to be the $A^1\tilde{A}_2 - \tilde{X}^1 A_1$ forbidden electric dipole transition ($n \rightarrow \pi^*$) characteristic of carbonyl compounds. The inclusion of configuration interaction modifies the energy of the $\tilde{A}^1 A_2$ state only slightly. Hence, this state can be described fairly accurately in terms of a single configuration ($\sim 91\%$) – the one arising from the promotion of an electron from the $7b_2$ orbital to the unoccupied $3b_1$ orbital. The remaining contribution to this state is made up of the configurations arising from the promotions $7b_2 \rightarrow 4b_1$ and $6b_2 \rightarrow 3b_1$. The $7b_2$ molecular orbital is essentially the oxygen $2p_y$ lone pair orbital (65%). The remaining contribution to this molecular orbital is from σ type atomic orbitals of the $(CN)_2C$ framework. The $3b_1$ and $4b_1$ orbitals are antibonding out-of-plane π^* orbitals composed of the $2p_x$ atomic orbitals on each nucleus. The $3b_1$ orbital is antibonding w.r.t. the C=O and C≡N chromophores but slightly bonding w.r.t. the CCC skeleton. $4b_1$ is the highest unoccupied out-of-plane π^* orbital and is antibonding w.r.t. all adjacent nuclei. The bond indices calculated for the $\tilde{A}^1A_2$ state are 2.70, 0.98 and 1.52 for the C≡N, C–C and C=O bonds which represents a decrease of 6.3%, 3.9% and 17.4% respectively from the ground state values. Hence, the result of an excitation to this state would be a pronounced weakening of the C=O bond and an increase in its bond length. Experimentally, this increase is manifested in the appearance of a long progression of the carbonyl stretch in the $n-\pi^*$ transition observed between 24390 and 38461 cm^{-1}. This stretching frequency has decreased to 1250 cm^{-1}. The oscillator strength for this transition was reported as 0.85×10^{-4}.

The next two lowest transitions are classified as $^1A_2 - \tilde{X}\,^1A_1$ and $^1B_1 - \tilde{X}\,^1A_1$ respectively. The $^1A_2$ state is a linear combination of the configurations arising from the promotions $6b_2 \rightarrow 3b_1$ and $10a_1 \rightarrow 2a_2$. The $6b_2$ and $10a_1$ orbitals are best described as in-plane π bonding orbitals localized on the C≡N group. $2a_2$ is an antibonding π^* out-of-plane orbital localized on the C≡N group. The $^1B_1$ state is quite similar to the above $^1A_2$ state.

No transitions are experimentally observed in this region. The transitions are either too weak to be observed which agrees with the low value of the calculated oscillation strengths or they may form part of the continuous absorption beginning at 43000 cm^{-1}. Wierzchowski *et al.* have reported predissociation in the lowest $n \rightarrow \pi^*$ transition $\tilde{A}\,^1A_2 - \tilde{X}\,^1A_1$. They postulate that this is caused by a dissociative state lying close to the $\tilde{A}^1A_2$ state. The state causing this predissociation is perhaps the second $^1A_2$ state at 39434 cm^{-1}.

The strong quasi-continuous absorption beginning at 43000 cm^{-1} has previously been assigned to either a $^1A_1 - \tilde{X}^1A_1(\pi \rightarrow \pi^*)$ or a $^1B_2 - \tilde{X}^1A_1(n \rightarrow \sigma^*)$ transition. Our calculations give two transitions in this region; one at 43578 cm^{-1}, $^1B_2 - \tilde{X}^1A_1(\pi \rightarrow \pi^*)$; and the other at 44040 cm^{-1}, $^1A_1 - \tilde{X}^1A_1(\pi \rightarrow \pi^*)$. The latter transition has an oscillator strength approximately ten times that of the former. Our calculations tend to rule out the assignment of the transition as $n \rightarrow \sigma^*$; our calculated values for transitions of this type are all too high in energy. Since the observed transition is strong, we prefer to assign it as $^1A_1 - \tilde{X}^1A_1$ $(\pi \rightarrow \pi^*)$, a transition localized on the C≡N chromophore. The $^1A_1$ and $^1B_2$ states are a mixture of configurations (see Table 3). $11a_1$ and $2a_2$ are antibonding π^* orbitals localized on the C≡N group. The latter consists of the out-of-plane $2p_x$ orbitals while the former uses the in-plane $2p_y$ and $2p_z$ orbitals. $1a_2$ is an out-of-plane bonding π orbital localized on the C≡N group. The $2b_1$ is an in-plane bonding π orbital bonding w.r.t. C and N; slightly bonding w.c.t. C and O; and antibonding w.r.t. the carbon nuclei.

The next two calculated transitions fall at 47023 cm^{-1}, $^1A_2 - \tilde{X}^1A_1$, and at 47034 cm^{-1}, $^1B_1 - \tilde{X}^1A_1$. Both are $\pi \rightarrow \pi^*$ transitions localized on the C≡N chromophore and both have oscillator strengths of zero. One would predict that they might be too weak to be observed but perhaps could be correlated with the weak bands reported at 48656, 48749 and 48831 cm^{-1}.

The resolved transition between 46900 and 63000 cm^{-1} has an oscillator strength of approximately 0.07. This transition could possibly be correlated with the transition calculated at 54780 cm^{-1}, $^1B_2 - \tilde{X}^1A_1(\pi \rightarrow \pi^*)$. Experimentally, maximum absorption occurs around 53000 cm^{-1}. By the Franck-Condon principle, this would correspond to the vertical transition – the transition which is calculated. The computed oscillator strength of 0.008 agrees with the experimental findings that the transition is weak. The $^1B_2$ state is mainly composed of the single configuration corresponding to $7b_2 \rightarrow 11a_1$. $11a_1$ is an in-plane π^* orbital localized on the CN group.

Duncan and Whitlock [3] observe a prominent transition at 57600 cm^{-1} which cannot be fitted into their vibrational analysis. Our calculations suggest that this band may be caused by another electronic transition as well as the two weak shoulders just above 60000 cm^{-1}. We calculate transitions at 58183, 60260, and 62240 cm^{-1} corresponding to the transitions $^1B_1 - \tilde{X}^1A_1$, $^1A_1 - \tilde{X}^1A_1$ and $^1A_2 - \tilde{X}^1A_1$ respectively. These are all $n \rightarrow \pi^*$ and arise chiefly from the configurations $7b_2 \rightarrow 2a_2$, $7b_2 \rightarrow 8b_2$ and $7b_2 \rightarrow 4b_1$ respectively.

Beyond this point, a large number of electronic transitions are calculated to be present and probably correspond to the continuous absorption observed between 63000 and 78100 cm^{-1}, the limit of the experimental data to date.

Triplet spectra have also been calculated but are not reported here for two reasons. The first is that a number of the singlet and triplet transitions are calculated to have the same energy. The cause for this is that the singlet-triplet separation is directly related to the value of an exchange integral which for $n \rightarrow \pi^*$ transitions vanishes identically within the CNDO approximation causing the singlet and triplet states arising from such a transition to be degenerate. The second reason is that no singlet-triplet spectra have been reported and we have no data with which to correlate our results.

Discussion

In general, the agreement with the experimental results is good and the calculations should serve as a guide to further work. One should keep in mind, however, that the method is an approximate one and more experimental work is required to verify the results, especially, in the higher energy regions where a large number of transitions occur. The ground state equilibrium geometry was the only geometry used in the calculations. Further work is in progress on the study of the electronic structure of the molecule as a function of the molecular geometry in various states.

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