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Full-range Bond-order Dependence of Intramolecular Vibrations: Ethylene and Tetracyanoethylene

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For analogous normal vibrations in conjugated systems of a similar type a linear relationship often exists between vibrational frequencies and bond orders. We find that this linearity can, in principle, be extended to include conjugated systems in both excited electronic states and ionic states. This indicates that the linearity covers a full range of bond order conceivable for conjugated systems. Such an aspect of molecular vibrations gives a concise and sometimes decisive clue not only to vibrational assignments but also to structural analyses of conjugated systems in various electronic states. Symmetric C=C stretching vibrations of ethylene and tetracyanoethylene nicely illustrate this situation.

Although most of the constituent atoms contribute to every vibrational mode of a molecule, many of the modes behave as if they were properties of individual functional groups.[1] This effect leads to a characteristic infrared band which appears within a relatively narrow energy range for such functional groups as methyl, hydroxyl, and carbonyl. For conjugated systems vibrational energies have both σ- and π-components. Detailed analysis by Coulson and Longuet-Higgins showed that a force constant for a π bond is a function of π bond order and π bond polarizability.[2] However, the use of bond order alone often suffices to estimate the vibrational frequency.[3] Berthier *et al.* found that a characteristic frequency for a variety of aldehydes and ketones typically gives an excellent linear correlation with a bond order of the carbonyl group.[4]

It is widely known that, when a conjugated compound forms a molecular ion, its infrared and Raman spectra change markedly;[5-9] so do the bond orders. When a conjugated system is electronically excited, such vibrational frequencies as found in the electronic absorption bands often change from those of the ground-state species.[9] However, attempts to correlate these frequencies with the corresponding bond orders have scarcely been made. This kind of study has been restricted to neutral conjugated systems in the ground state, where a change in bond order is rather modest.[3] In this paper, I would like to show that a linear relationship between vibrational frequencies and π bond orders can, in principle, be extended to cases where both quantities change much more widely. Recall that a wide variation in π bond order can usually be realized in the following three ways: exciting a conjugated system of a molecule, removing one or more π electrons from a molecule, and attaching one or more π electrons to a molecule.

Results and Discussion

Ethylene is the simplest conjugated hydrocarbon. A vibrational frequency of the symmetric C=C stretching mode can be detected in the Raman spectrum. It is 1623 cm^{-1} in the ground electronic state.[10] This frequency is reduced to 850 cm^{-1} in the excited electronic state,[10] which is observed as a vibrational component of the first electronic absorption band around 45000 cm^{-1}. Some vibrational frequencies can be seen in a photoelectron spectrum of ethylene.[11] They are ascribed to the molecular cation $C_2H_4^+$. The first photoelectron band corresponds to a removal of a π electron from the single π-valence orbital. This band exhibits a 1230 cm^{-1} vibrational progression, which has been assigned to a symmetric C=C stretching mode of $C_2H_4^+$.

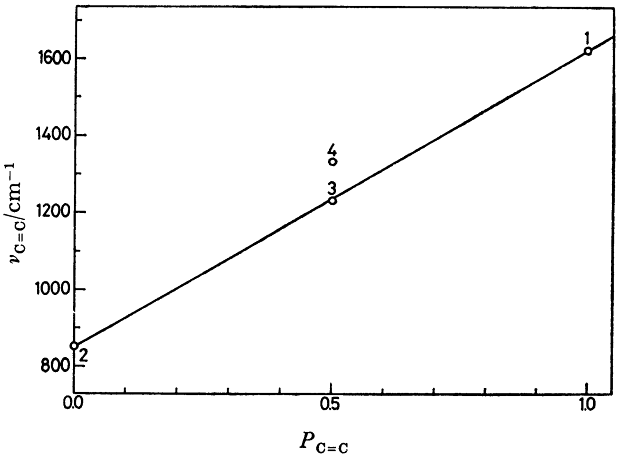

Fig. 1. Plot of $\nu_{C=C}$ *vs.* $P_{C=C}$ for ethylene: 1, C_2H_4; 2, C_2H_4*; 3, $C_2H_4^+$; 4, $C_2H_4^-$.

In order to see if these frequencies ($\nu_{C=C}$) correlate with the corresponding C=C π bond orders ($P_{C=C}$), the former quantities are plotted against the latter ones in Fig. 1. The C=C π bond orders are 1.000 for C_2H_4, 0.000 for C_2H_4*, and 0.500 for $C_2H_4^+$, where C_2H_4 and C_2H_4* denote the ground and excited electronic states of ethylene, respectively. C_2H_4 and C_2H_4* are chosen to draw a reference line in Fig. 1 because the number of π electrons are kept constant. This line is expressed as

$$\nu_{C=C} = 773.0\,P_{C=C} + 850.0. \qquad (1)$$

Here, it is surprising to see that this linear relationship can exactly be applied to $C_2H_4^+$. Note that C=C π bonds of C_2H_4, C_2H_4*, and $C_2H_4^+$ cover the full range of π bond order conceivable for conjugated systems.

In 1973 Sanche and Schultz reported an electron transmission spectrum of ethylene in the gas phase.[12] The first band exhibits an average vibrational spacing of 1330 cm^{-1}, which most likely results from a symmetric

C=C stretching vibration of an ethylene anion ($C_2H_4^-$). The C=C π bond order of $C_2H_4^-$ must be the same as that of $C_2H_4^+$. However, this anion is placed about 100 cm^{-1} above the reference line in Fig. 1. This implies that the C=C bond in $C_2H_4^-$ is a bit more stabilized than expected from Eq. 1.

An analogous symmetric C=C stretching mode of tetracyanoethylene (TCNE) gives another good example which supports a wide-range π-bond-order dependence of vibrational frequencies. A Raman spectrum of this compound shows that the vibrational frequency of 1569 cm^{-1} can be assigned to the symmetric C=C stretching mode.[13,14] This frequency is nearly comparable to that of C_2H_4. TCNE exhibits the first electronic absorption band in the energy range 35000—43000 cm^{-1} in the gas phase. Spacings of the vibrational components are irregular, and the 0-1 level seems to be shifted, probably due to an intersection of the two potential surfaces.[15] Its average 1128 cm^{-1} spacing was assigned to the symmetric C=C stretching mode of the excited TCNE molecule (TCNE*).

TCNE is a typical electron acceptor with an electron affinity of 2.89 eV.[16] Therefore, its monoanion (TCNE$^-$) is considerably stabilized,[17] forming many anion radical salts[18] in the form M$^+$TCNE$^-$. For these salts it is striking that there appears intense absorption at about 1370 cm^{-1} in a region barren of significant absorption by TCNE.[19] This has been assigned to the totally symmetric C=C stretch which became infrared active by the Ferguson-Matsen mechanism.[20] This interpretation was later justified by a Raman spectroscopic study.[14] The C=C stretch of TCNE$^-$ is influenced by the cation to some extent. Thus C=C stretching frequencies are 1387 cm^{-1} for the lithium, 1390 cm^{-1} for the sodium, 1371 cm^{-1} for the potassium, and 1358 cm^{-1} for the cesium salt.[21] The first absorption band of TCNE$^-$ in solution exhibits numerous vibrational maxima. Unfortunately, the average spacing of 530 cm^{-1} should rather be assigned to the symmetric C–C stretch.[22]

Recently, Khatkale and Devlin prepared TCNE^{2-} and TCNE^{3-} by vacuum condensation methods[23] and measured infrared and Raman spectra of the four molecule series TCNE, TCNE$^-$, TCNE^{2-}, and TCNE^{3-}. Symmetric C=C stretching frequencies are 1392, 1256, and 1346 cm^{-1} for the sodium salts of TCNE$^-$, TCNE^{2-}, and TCNE^{3-}, respectively. A photoelectron spectrum of TCNE has been reported by three research groups.[24–26] Stafast and Bock analyzed it[26] and attributed the 1360 cm^{-1} progression of the first band to the symmetric C=C stretch of TCNE$^+$. An uncertainty of $\pm$100 cm^{-1} may be included in this experimental frequency.[24–26]

π Bond orders of the TCNE series were calculated using Coulomb and resonance integrals suggested by Orgel and coworkers.[27] A Coulomb integral for a cyano nitrogen was set equal to $\alpha+\beta$, and a resonance integral for the C≡N bond to 1.2β. The C=C π bond orders thus calculated are 0.700 for TCNE, 0.314 for TCNE*, 0.491 for TCNE$^+$, 0.523 for TCNE$^-$, and 0.347 for TCNE^{2-} and TCNE^{3-}. The C=C stretching frequencies are then plotted against the corresponding bond orders in Fig. 2, where a reference line crosses two points representing TCNE and TCNE*. This line is expressed as

$$\nu_{C=C} = 1142.5\, P_{C=C} + 769.6. \qquad (2)$$

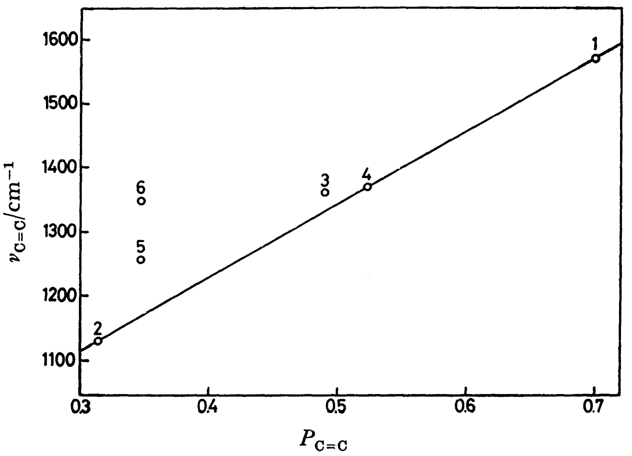

Fig. 2. Plot of $\nu_{C=C}$ *vs.* $P_{C=C}$ for tetracyanoethylene: 1, TCNE; 2, TCNE*; 3, TCNE$^+$; 4, TCNE$^-$; 5, TCNE^{2-}; 6, TCNE^{3-}.

As seen from Fig. 2, both TCNE$^+$ and TCNE$^-$ are also located near this line. Some other cyanoethylenes appear to behave analogously, although data for the electronically excited species are lacking. The C=C stretching frequencies are 1615 cm^{-1} for acrylonitrile (0.886), 1360 cm^{-1} for its cation (0.515), 1594 cm^{-1} for 1,1-dicyanoethylene (0.806), and 1360 cm^{-1} for its cation (0.523).[26] Here, values in parentheses are the appropriate π bond orders.

We hence feel confident that a linear bond-order dependence of the C=C stretching frequency exists among a variety of electronic states. Note that the C=C π bond order in our case changes within a range of 0.000—1.000, while in the case of aldehyde and ketones[3,4] the C=O π bond order changes modestly, in the range 0.819—0.958. Khatkale and Devlin reported that a plot of the empirical force constant *vs.* bond order is nearly linear for tetracyanoquinodimethane anions (TCNQ^{n-}).[28] This fact also supports a universality of such linearity as Eqs. 1 and 2 indicate.

Unfortunately, some exceptional species are found in Fig. 2. As in the case of $C_2H_4^-$, higher anions of TCNE show considerably larger frequencies than expected from Eq. 2. The C=C stretching frequency of TCNE^{2-} deviates upward from the reference line by 90 cm^{-1} and that of TCNE^{3-} by 180 cm^{-1}. It is especially noticeable that the C=C stretching frequency of TCNE^{3-} is somewhat larger than that of TCNE^{2-}. The effect of the third π electron added is apparently quite different. This electron is expected to enter an orbital which is nonbonding in the C=C region, so an apparent strengthening of the C=C bond was not anticipated.[23] Accordingly, it is quite natural to consider some possible mechanism which intensifies the C=C bond strength.

We have assumed that skeletal structures of all molecular species are identical with that of a neutral molecule. This may be true for TCNE* and TCNE$^+$ since the 0-0 vibrational component of the first band is strongest in the electronic absorption spectrum of TCNE[15] and in its photoelectron spectrum.[26] The same situation applies to the ethylene cation.[11] However, there is no reason to believe that the same situation must apply to the other species, especially to higher anions of TCNE.

On the other hand, it is not difficult to imagine that additional π electrons in the TCNE anions are highly delocalized with high polarizability. Perhaps more reasonable is the assumption that the structures of the dianion and the trianion are strongly distorted by asymmetric cation polarization fields, such that the original TCNE D_{2h} symmetry is no longer useful for the purpose of vibrational analyses.[23] According to Jeanmaire *et al.*,[22] the electrogeneration of $TCNE^{2-}$ in acetonitrile containing tetrabutylammonium perchlorate seemed to be electrochemically quasireversible. They speculated that the cause of the quasireversible electron transfer to form the dianion is due to a geometry change and that $TCNE^{2-}$ is a nonplanar species even in solution.[22] Such a tendency toward nonplanarity may be enhanced in $TCNE^{3-}$. For these reasons, we cannot always take the premise that the molecular ion series might constitute such a set of molecular ions that vibrational assignments for the other members would follow smoothly from a firm assignment of the modes of one member of the series. Significant deviation of a vibrational frequency from the reference line should be interpreted as due to a molecular deformation or some other geometry change. However, this does not deny our view that the bond-order dependence of vibrational frequencies holds widely because bond orders are necessarily modified for the deformed species.

A conjugated system of TCNE is fairly large compared with that of ethylene, so $TCNE^-$ appears to retain the geometry of its neutral species. However, it may be impossible for the ethylene monoanion to retain the ground-state geometry of the neutral species because of its compact conjugated system. The deviation of $100\ cm^{-1}$ apparently indicates the degree of extra stabilization of the C=C bond.

I previously observed a vibrational structure in the charge-transfer (CT) absorption band of the naphthalene–TCNE complex in various saturated hydrocarbons.[29] The vibrational frequency was 1300—1400 cm^{-1}. Similar frequencies are found in the solid-state absorption spectra of several aromatic hydrocarbon–TCNE complexes.[30,31] According to Kadhim and Offen,[30] such vibrational frequencies might be characteristic of the acceptor molecule because a CT transition is naively viewed as an electron jump to the lowest unoccupied orbital of the acceptor. The appearance of a 1300—1400 cm^{-1} vibration thus indicates that the TCNE component in the complex is almost completely ionized in the CT excited state since the frequency is close to that of $TCNE^-$ in Fig. 2. On the other hand, the resonance Raman spectrum of TCNE in benzene[32] exhibits a strong line at 1565 cm^{-1}, and that of TCNE in anisole[33] at 1556 cm^{-1}. These frequencies suggest that the ground-state TCNE complexes with benzene and anisole are essentially nonionic, in accord with the prediction by simple CT theory.[34]

Concluding Remarks

As has been examined above, a linear bond-order dependence of vibrational frequencies can, in principle, be extended to a conjugated system in any electronic state. This aspect of intramolecular vibrations can be used to assign not only electronic absorption bands but also photoelectron bands of various conjugated systems. In this connection, Ikemoto *et al.* observed a 1530 cm^{-1} vibrational component in the first photoelectron band of TCNE,[24] and assigned it to the symmetric C=C stretch. However, the frequency of this mode is predicted from Eq. 2 to be close to 1330 cm^{-1}. In this sense the frequency read by Stafast and Bock (1360 cm^{-1})[26] appears more reasonable. If a given vibrational mode deviates to a higher energy side, this should be regarded as a significant indication of a geometry change, and some possible stabilizing mechanism must be considered for the species concerned. Thus the relationship established between π bond orders and vibrational frequencies will give an important and sometimes decisive clue to structural chemistry of conjugated systems, especially when other experimental data are scanty.

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