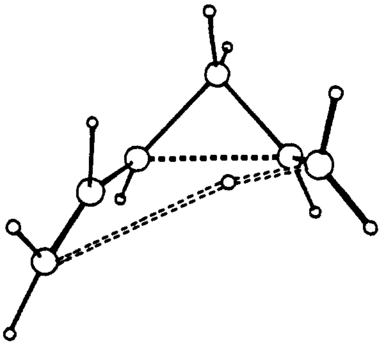
CH bond with the breaking CC bond of the cyclopropane ring, as shown in Figures 4C,D and 5C,D. Small movement of the transferring hydrogen occurs in TS-endo. The CH breaking bond length is 1.351 Å in the endo transition structure. Here, little distortion from reactant is required in order to orient the molecule so that the hybridized orbital of C_4 aligns with the hybridized orbital on C_5 (see Figure 5C). Figure 4D shows a Newman projection along the C_1C_6 bond of TS-endo. As sketched in the corresponding orbital representation in Figure 5D, the π-orbital of C_1 is oriented as to maximize overlap with the orbital of C_6 of the developing double bond, while still maintaining π bonding with the hybrid orbital on C_2.

If we imagine a 180° rotation about the C_1C_6 bond, to produce the exo transition structure from TS-endo, structure **7** is obtained. This clearly has C_2 very far from the H, so that significant bonding between C_1 and the transferring H is not possible without significant distortion of the allyl moiety.



7

In the resulting exo transition structure, the overlap of the hybrid orbitals on C_4 and C_5 is diminished somewhat (Figure 5E). In order to have overlap of the hydrogen 1s orbital with a p orbital at C_2, which now points away from the cyclopropane ring in this transition structure (Figure 4E), and still have overlap of the hybrid orbitals on C_4 and C_5, the CH breaking is much more advanced (1.446 Å). The nature of this distortion, which is brought about by the need to complete the hydrogen transfer, is easily seen by the staggered position of the methyl group and is reflected by the similar-forming CH bond lengths of 1.480 and 1.453 Å for TS-endo and TS-exo, respectively. As seen in Figure 4F and 5F, the π-orbital of C_1 is again oriented to maximize overlap of the developing double bond while maintaining overlap of the hybrid orbital of the former double bond.

The orbital overlap argument used to explain the origin of the endo preference of reaction can also be rephrased to focus on the conformational preference of a double bond in a seven-membered ring. The endo transition structure with the developing C_1C_6 double bond is analogous to a seven-membered ring containing a cis double bond, while the exo transition structure is analogous to a seven-membered ring with a trans double bond. In both transition structures, the C_1C_6 bond is about 65% double bond in character in comparison to the geometries of reactant **1** and products. In this respect the endo preference is easily understood as equivalent to the preference of a cis double bond, rather than a trans double bond in a seven-membered ring. The 17 kcal/mol difference results from the strain in forming the seven-membered ring in the exo transition state.

An interesting feature of TS-endo is that the Mulliken charge on the transferring hydrogen is 0.27 electron. This value is intermediate between the charge found on hydrogen in concerted 1,5-sigmatropic hydrogen shifts of 1,3-pentadiene (0.22) and 1,3-cyclopentadiene (0.31).[17] The Mulliken charge on the transferring hydrogen of TS-exo is much less at a value of 0.22. This implies a "tighter" transition state for the endo transformation,[17] which proceeds at a faster rate as compared to TS-exo.

Acknowledgment. We are grateful to the National Science Foundation and to the Harris Corporation for financial support of this research. We also thank Dr. Julius Rebek, Jr. and Weston T. Borden for discussions and their inexpensive intuitions ("it is a trans double bond in a seven-membered ring").

Registry No. 1, 2628-57-1.

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(17) Kahn, S. D.; Hehre, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291-8292.

Electronic Spectra and Chemical Reactivity

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Abstract: Perturbation theory suggests a close relationship between the electronic spectra of molecules and energy barriers to possible unimolecular and bimolecular reactions. Considering only ν_{max}, the vertical frequency of the lowest excited state (of the same multiplicity), a number of interesting correlations can be made. It is necessary (a) to compare only groups of related molecules and (b) to use elementary spectroscopic theory to identify the nature of the lowest excited state. The relationship between vis-UV spectra and the stability of isomers is discussed.

For some chemists the presence of color in a molecule is an indication of reactivity, e.g. free radicals, but there are enough stable colored species to make the generalization of dubious value. Nevertheless, the vis-UV spectrum of a substance should contain much useful information about its chemical behavior. Certainly a detailed analysis of the spectrum in terms of the usual MO theory would yield information on valence shell MO's. Since chemical reactivity can also be discussed in terms of MO theory, a close connection must exist.

When detailed analysis is not available, what information can be gained from the gross features of the spectrum? The most obvious feature is the first absorption band, defining the lowest energy excited state. The purpose of this article is to show what information on chemical reactivity is contained in this band and to point out the pitfalls in the interpretation.

Table I contains the experimental data for a number of common, polyatomic molecules. The sources are the admirable reviews by Herzberg[1] and by Robin.[2] The convention is adopted of

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(1) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1967.

(2) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: New York, Vol. I, 1974; Vol. II, 1975; Vol. III, 1985.

(3) Note that Herzberg gives estimated term values for the equilibrium geometry of the excited state. These can differ substantially from ν_{max}. An extreme example is CO_2, where ν_{max} = 68 000 cm^{-1}, but the term value for the bent configuration in excited CO_2 is only 46 000 cm^{-1}.

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Table I. Vertical Frequencies of the First Absorption Band of Selected Molecules in the Vapor Phase[a]

molecule	ν_{max}, × 10^3 cm^{-1}	molecule	ν_{max}, × 10^3 cm^{-1}
CH_4	78.2	CH_3CN	60.0
C_2H_6	75.8	$CH_2{=}CHCN$	47.5
n-C_5H_{12}	64.0	$CH_2{=}CO$	25.9
i-C_5H_{12}	64.0	$CH_2{=}N_2$	21.2
CH_3F	75.4	HCOOH	45.5
CH_3Cl	59.0	$HCOOCH_3$	47.5
CH_3Br	50.0	CH_3COOH	47.5
CH_3I	38.5	$HCONH_2$	45.5
t-C_4H_9I	37.0	HCOF	45.5
CH_3OH	54.5	CH_3COCl	42.6
C_2H_5OH	55.0	CH_3NO_2	37.0
t-C_4H_9OH	55.0	C_2H_2	57.0
$(CH_3)_2O$	54.4	C_2H_4	61.4
THF	50.0	C_3H_6	58.0
HCHO	31.0	$(CH_3)_2C{=}C(CH_3)_2$	53.5
CH_3CHO	34.0	$CH_2{=}CHCH{=}CH_2$	48.3
CH_3COCH_3	35.0	C_6H_6	40.0
$CH_2{=}CHCHO$	26.5	CF_4	110.5
C_6H_5COOH	36.0	BF_3	63.6
C_6H_5OH	37.00	BCl_3	57.9
$C_6H_5NO_2$	37.00	$Cr(CO)_6$	31.5
C_5H_5N	40.3	RuO_4	26.0
H_2O	60.4	OsO_4	34.0
CO_2	68.0	BH_2	13.0
NH_3	51.5	NH_2	15.4
$(CH_3)_3N$	44.2	HCO	15.2
PH_3	55.6	NCO	25.0
H_2S	50.0	NO_3	17.2
$(CH_3)_2S$	43.9	CH_3	46.3
SF_6	93.0		

[a] Same multiplicity as ground state. Data from ref 1 and 2.

expressing all data in energy units of 10^3 cm^{-1}. For convenience, 10^3 cm^{-1} = 2.86 kcal/mol, and 50 × 10^3 cm^{-1} corresponds to 2000 Å. The data refer to the lowest energy transition to a state of the same multiplicity as the ground state. The quantity given is ν_{max}, the frequency of the most intense band in the Franck–Condon envelope, or the vertical frequency. There restrictions, as we shall see, are required by theory.

Only spectroscopic data in the vapor phase are used. It is irrelevant whether the transition is dipole allowed or forbidden. The intensity of the band is not a factor. The bands discussed are all observed bands, but in one or two cases it may be necessary to postulate that an unobserved electronic transition exists at lower energy than any yet found. In such cases, reasons for the failure to observe must be given.

The term chemical reactivity should be defined. It turns out that the spectral data give information on energy barriers, and therefore it is kinetic reactivity that is meant. There is no direct information on thermodynamic stability, but sometimes this can be inferred.

The kinds of chemical reactions must also be limited. They should be reactions that require a substantial rearrangement of the original electronic distribution of the reactant molecule. For unimolecular reactions these would be dissociation or isomerization reactions. For bimolecular reactions there must be substantial electron transfer, in one or both directions, and usually internal rearrangements as well. Simple electrostatic bonding between two molecules or ions is not covered. Also complete electron transfer between two isolated molecules is not covered, since this depends only on thermodynamic factors.

Theory

Perhaps the first modern attempt to correlate electronic spectra with reactivity was due to Walsh.[4] He pointed out that cyclopropane starts absorbing at 1950 Å, which is very similar to ethylene and quite different from paraffin hydrocarbons, such as propane, which only starts to absorb at 1400 Å. At the same time cyclopropane is very reactive, compared to propane, and behaves very much more like the olefins. Walsh's explanation was that cyclopropane, like ethylene, had loosely held electrons in its valence shell. Ionization potentials, determined later, bore this out: propane, 10.95 eV; propene, 9.74 eV; cyclopropane, 10.10 eV.

The modern theory of chemical reactions gives a more detailed and somewhat different explanation. Quantum mechanical second-order perturbation theory is the basis, and various formulations may be used.[5] For the present purpose, the method based on the second-order Jahn–Teller effect is most appropriate.[6]

We start with a collection of nuclei and electrons at some point Q_0 representing an initial nuclear configuration. The wave equation is assumed to be solved giving rise to a number of eigenvalues E_0, E_1, ..., E_k, and the corresponding electronic eigenstates ψ_0, ψ_1, ..., κ_k. We now move the nuclei a small distance Q along the reaction coordinate. The new ground-state energy is now calculated by second-order perturbation theory.

After distortion the Hamiltonian may be written as a Taylor–Maclaurin series where H_0 is the original Hamiltonian, U is

$$H = H_0 + \left(\frac{\partial U}{\partial Q}\right)Q + \tfrac{1}{2}\left(\frac{\partial^2 U}{\partial Q^2}\right)Q^2 \ldots \tag{1}$$

the nuclear–nuclear and nuclear–electronic potential energy, and Q is the small displacement along the reaction coordinate. We truncate the series at Q^2.

The energy becomes

$$E = E_0 + \left\langle \psi_0 \middle| \frac{\partial U}{\partial Q} \middle| \psi_0 \right\rangle Q + \left\langle \psi_0 \middle| \frac{\partial^2 U}{\partial Q^2} \middle| \psi_0 \right\rangle \frac{Q^2}{2} + \sum_k \frac{\left[\left\langle \psi_0 \middle| \frac{\partial U}{\partial Q} \middle| \psi_k \right\rangle Q \right]^2}{(E_0 - K_k)} \tag{2}$$

E_0 is the original energy at point Q_0, the next two terms are the first-order perturbation energy, and the last term is the second-order perturbation energy. The bracket symbol indicates integration over the electronic coordinates only.

At the same time the wave function changes from ψ_0 by mixing in the excited state wave functions:

$$\psi = \psi_0 + \sum_k \frac{\left\langle \psi_0 \middle| \frac{\partial U}{\partial Q} \middle| \psi_k \right\rangle Q}{(E_0 - E_k)} \psi_k \tag{3}$$

Note that only excited states of the same multiplicity can be mixed. Also ψ_k and E_k must be those for the ground-state nuclear positions.

The first-order perturbation energy simply averages the effect of changing the nuclear positions over the original electronic distribution. The second-order perturbation energy is an effect due to a change in the electron distribution. This change is called the transition density. Clearly this lowers the energy, as can be seen in (2). The quantity $(E_0 - E_k)$ always has a negative value. Both E_0 and E_k are negative, for bound states, with E_0 having the greater magnitude.

There are important symmetry restrictions contained in eq 1–3, but these are not important at this time. What is important is that a chemical reaction (changing nuclear positions) cannot occur unless the last term in (2) has an appreciable value. This will be more likely as the transition energies, $(E_0 - E_k)$, have smaller values. Large values of $(E_0 - E_k)$ will mean a large energy barrier to all changes.

In eq 2 and 3, there is a sum over all excited states. However, only a few will be useful in driving the reaction. In MO terms, the most important states will be those in which an electron is promoted from a filled MO to an empty MO, both in the valence

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[4] Walsh, A. D. *Trans. Faraday Soc.* **1949**, 179–181.

[5] For example, see: Klopman, G. *Chemical Reactivity and Reaction Paths*; Wiley-Interscience: New York, 1974. Salem, L. *Electrons in Chemical Reactions*; Wiley-Interscience: New York, 1982.

[6] Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164–1169. Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976.

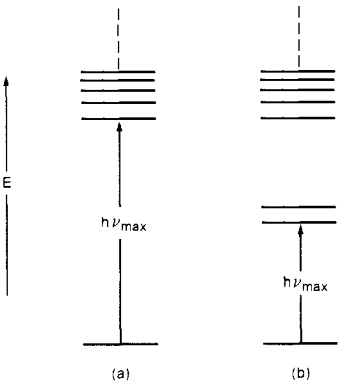

Figure 1. (a) Stable molecule with large energy gap between ground state and excited states. (b) Stable molecule with small energy gap for excited states that are not chemically useful.

shell. The MO's are selected to correspond to the old bonds that are to be broken and the new bonds that are to be made during the reaction. For bimolecular reactions, the important states are those in which electrons are promoted from filled MO's in one reactant to empty MO's in the other.

In simple MO theory the HOMO and the LUMO (the frontier orbitals) define the lowest energy transition. They are also the orbitals that drive the chemical reaction.[7] In actuality, neither of these statements need be true. However, as a general rule, it is expected that the excited states that drive the reaction will lie close to the first excited state. Thus we will have

$$h\nu_{max} = E_1 - E_0 \simeq E_k - E_0 \quad (4)$$

where the k identifies the chemically significant states.

Figure 1a helps to explain this reasoning. It shows the ground state and some of the lowest excited states on an energy scale. In practice there will be a dense manifold of excited states, some of them chemically significant and others not. The value of $h\nu_{max}$ sets a lower limit to all of these. Also, as a rule, $h\nu_{max}$ is very much greater than the differences in energy between the lowest lying states. There observations justify the approximation of eq 4. If we compare a series of similar molecules, we can usually expect that variations in ν_{max} will be larger than variations in the differences between the lowest excited state and the chemically important ones.

A case where ν_{max} becomes quite small is shown in Figure 1b. This could represent a colored molecule. If the first excited state in this case is chemically significant, then great chemical reactivity is predicted. But if this is not the case, we have no firm basis for prediction. The chemically important states may lie near the first excited state or still be high in energy, as shown.

Some Correlations. Some free radicals are included in Table I to make the point that most transient species, which we cannot see, would be colored, if we could see them. The low-lying transitions of these radicals almost invariably involve a half-filled orbital (SOMO) in the valence shell. The most common reaction is to fill the hole in the valence shell by forming a bond. High reactivity is expected, consistent with the spectra.

Since the electronic spectrum gives only differences in energy between states, it is not a basis for assigning electronic energies or thermodynamic stabilities, but information can be obtained on closely related properties, such as bond dissociation energies, and relative energies of isomers.

For diatomic molecules the only possible unimolecular reaction is dissociation into atoms or ions. Figure 2 shows plots of dissociation energies into atoms, D_0, versus term values for the lowest excited singlet states for two groups of diatomic molecules.[8] The first are univalent, ionic molecules such as NaBr, LiH, and TlF. The second group consists of singly bonded, covalent molecules, such as H_2, Na_2, Cu_2, Cl_2, and HF.

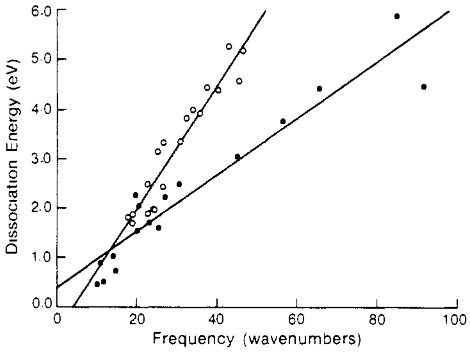

Figure 2. Dissociation energy (eV) plotted against ν_{max} (×10^3 cm^{-1}). Open circles, ionic diatomic molecules; filled circles, covalent diatomic molecules.

Table II. Spectral and Other Data for the Hydrides of the Nonmetals

	CH_4	NH_3	H_2O	HF
ν_{max}, × 10^3 cm^{-1}	78.2	51.5	60.4	85.0
I, eV	12.7	10.7	12.6	16.0
D_0, kcal	105	107	119	136
	SiH_4	PH_3	H_2S	HCl
	72.5	55.6	51.3	65.5
	11.7	10.0	10.5	12.7
	90	87	91	103
	GeH_4	AsH_3	H_2Se	HBr
	69.4	54.7	50.8	56.4
	11.3	10.0	9.9	11.7
	~80[a]	80	79	88
		SbH_3	H_2Te	HI
		50.7	50.0	45.0
		9.6	9.1	10.5
		~68[a]	~67[a]	71

[a] Estimated from mean dissociation energy of hydride. Data from ref 27 and 28.

For the ionic molecules, the slope, in dimensionless units, is exactly one, and the correlation coefficient is 0.959. For the covalent molecules, the slope is 0.46, and the correlation coefficient is 0.950. For both series of molecules, the excited state needed for dissociation is from the ($\sigma \rightarrow \sigma^*$) transition,[9] but the lowest observed state is more likely to be a ($n \rightarrow \sigma^*$) or ($\pi^* \rightarrow \sigma^*$) transition. The observed correlation is remarkable, under these conditions.

The halogens provide a useful example of the unreliability of color as a guide to stability. The sequence of colors, yellow, green, red, and violet, suggests a regular sequence with F_2 the most stable, and I_2 the least stable. But fluorine is well known to have an unexpectedly small value of D_0. The colors of the three heavy halogens, it turns out, are due to triplet-state excitations.[10] Because of the heavy-atom effect, these are quite intensive, but for F_2 the triplet band is too weak to be observed. The correct singlet states fall in the same order as the D_0 values (Figure 2).

The most common bimolecular reaction would be the partial transfer of a pair of electrons to form a coordinate, covalent bond between two molecules. This is the generalized acid–base reaction

$$A + :B \rightarrow A:B \quad (5)$$

Typically there is some electron transfer in both direction, σ- plus π-bonding. Table II contains the values of ν_{max}, the ionization potential, I, and the bond dissociation energy, D_0, for the hydrides of the nonmetallic elements. D_0 refers to the dissociation of the first hydrogen atom. I is a measure of the electron-donating ability of the molecule.

Except for group 15, there is perfect correlation between ν_{max} and both I and D_0, as one goes down the group. As ν_{max} decreases,

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(7) Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1984–1997.

(8) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(9) Reference 7, pp 22 and 50.

(10) Rees, A. L. G. *J. Chem. Phys.* **1957**, *26*, 1567–1571.

the reactivity, both for dissociation and for acting as a Lewis base, increases. Group 15 is abnormal in that ν_{max} is greater for PH_3 and AsH_3 than for NH_3. The values of I also did not fall as fast with increasing molecular weight. Only for group 15 is a second unimolecular reaction known, the inversion reaction. The barrier to inversion is very small for NH_3 (5.6 kcal) and much larger for PH_3 (27 kcal), AsH_3 (34 kcal), and SbH_3 (29 kcal).[11] The values of ν_{max} reflect a compromise between correlating with D_0 (greatest for NH_3) and the inversion barrier (greatest for AsH_3).

Further consideration of the first excited states is useful. For all the molecules of Table II, the terminating state is believed to be Rydberg in character.[2] The transitions are all (n → R), except for group 14 where it is necessarily $\sigma \rightarrow$ R. The first states are not chemically active, therefore, but it is obvious that the necessary $\sigma \rightarrow \sigma^*$ states must lie close to them to correlate with D_0. Also the originating orbital must be the orbital that loses an electron most readily, correlating with I, and also with Lewis base behavior.

The transition that drives the inversion reaction is the n $\rightarrow \sigma^*$,[11] which must also lie close to the first band. It may seem incongruous to invoke a state lying more than 51 500 cm^{-1} above the ground state as being important for the very rapid ammonia inversion, $\nu = 10^{10}$ s^{-1}, but this kind of reaction requires only modest electron density reorganization. In addition, tunneling bypasses the requirement for the planar configuration.

Numerous other examples exist where ν_{max} correlates with bond strength. A good example is the series CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$.[12] Unlike the data in Table II, it is $SiCl_4$ that has the largest value of ν_{max}, in line with the fact that the Si–Cl bond is stronger than the C–Cl bond. A similar inversion is expected for CF_4 and SiF_4.

Molecules with very weak bonds should reflect this in their vis–UV spectra. H_2O_2 and N_2H_4 are two such molecules. Unlike H_2O and NH_3 whose absorptions cut off sharply, the two unstable molecules have long, continuous first absorptions, of low intensity and extending well past 2200 Å.[13] This behavior is characteristic of repulsive excited states. The maxima cannot be located.

Ethylene oxide, C_2H_4O, is a very reactive molecule, undergoing ring-opening reactions readily. Walsh attempted to explain this by comparing its spectrum to that of cyclopropane.[4] However, the correct comparison must be to other ethers. The first absorption band of C_2H_4O is at 58.4 × 10^3 cm^{-1}, and that of $(CH_3)_2O$ is at 54.4 × 10^3 cm^{-1}, which leaves the reactivity of the former unexplained.

The answer in this case is that there is a low-lying state of ethylene oxide, but it is spectroscopically unobservable. It has been discussed theoretically.[14] The state is due to a $(\sigma \rightarrow \sigma^*)$ transition and has a ring-opened structure. The symmetry is A_2 in the C_{2v} point group, and the transition is therefore dipole forbidden. Combined with the repulsive nature of the state, which spreads out the weak intensity, the state will not be seen.

Besides giving information on unimolecular dissociation, the values of ν_{max} should relate to rates of reaction with other reagents. An example is provided by the methyl halides, where the values of ν_{max} fall steadily in the order $CH_3F > CH_3Cl > CH_3Br > CH_3I$. This is the order of decreasing bond strengths, as expected, but it is also the order of increasing rate of reaction with nucleophilic reagents.

The electronic transition in these cases are all (n $\rightarrow \sigma^*$), so that the observed correlations are sensible. The attack of a nucleophile puts electronic density into the σ^* orbital, which is the lowest in energy, that of the carbon–halogen bond. This is the terminating orbital in the first spectral band, as well.

The correlation cannot be pushed too far. Methyl nitrate and nitromethane have ν_{max} at 35 × 10^3 and 37 × 10^3 cm^{-1}, which suggest that they are even more reactive than CH_3I. But CH_3ONO_2 is actually less reactive than CH_3Cl in nucleophilic-substitution reactions, and CH_3NO_2 is very unreactive. The low-energy transitions are due to (n $\rightarrow \pi^*$) transitions residing in the NO_3 and NO_2 groups and have nothing to do with breaking a bond to carbon.

There are a number of molecules containing the carbonyl and nitrile groups in Table I. The values of ν_{max} refer in these cases to (n $\rightarrow \pi^*$) transitions of rather low intensity. The most characteristic reaction of these molecules is the addition of a nucleophilic reagent to the π^* orbital. The $(\pi \rightarrow \pi^*)$ transition helps to drive this reaction by opening the double bond to a zwitterionic state.

The (n $\rightarrow \pi^*$) transition is not directly active, but it gives indirect information. It has been shown that substituents affect the π^* orbital more than the n orbital.[15] Therefore, the order of ν_{max} is also the order of increasing energy for π^*. This, in turn, makes nucleophilic addition more difficult. The series $CH_3CN > CH_2{=}CHCN \sim HCOOCH_3 > HCONH_2 \sim HCOOH \sim HCOF > CH_3COCl > CH_3COCH_3 > CH_3CHO > CH_2O > CH_2{=}CHCHO$, with ν_{max} falling from 60.0 × 10^3 to 26.5 × 10^3 cm^{-1}, agrees very well with the tendency to undergo the addition of nucleophiles.

But caution is needed since CF_3COOH has the same ν_{max} as CH_3COOH, in spite of the well-known neffect of the CF_3 group in favoring addition to the carbonyl. Clearly the inductive effect of the group has affected both the n orbital and the π^* orbital equally.

The series from HF to CH_4 has reactivity increasing from HF to H_2O to NH_3, and then sharply decreasing at CH_4. A similar series can be formed from CH_4 (78.2 × 10^3 cm^{-1}), CH_3OH (54.5 × 10^3 cm^{-1}), CH_2O (31.0 × 10^3 cm^{-1}), HCOOH (45.5 × 10^3 cm^{-1}), and CO_2 (68.0 × 10^3 cm^{-1}). Thus, reactivity for the parent member of several important families of organic compounds is greatest at the aldehyde stage. Both methane and carbon dioxide are inert.[16] Thermodynamically, methane can be considered least stable of the series, since each member is oxidized exothermically to the next. The values of ν_{max} clearly correlate with kinetic stability, though this may be coupled with thermodynamic stability, as in the case of CO_2.

Isomerization. In view of the preceding, it is tempting to speculate that among isomeric compounds, the most stable isomer will have the largest value of ν_{max}. An examination of isomers such as C_2H_5OH and $(CH_3)_2O$, the butenes, or the butanes shows that there is no such relationship. The values of ν_{max} are large for all isomers and do not vary with relative stability. This result is expected, since the interconversion of these kinds of isomers would require complex mechanisms with large activation energies.

A different result is found if two isomers can be converted by a simple, one-step mechanism. Then it is required that the barrier be smaller for the less stable isomer. Examples would be linkage isomers. The isonitrile (ν_{max} = 54.9) isomerizes on heating to

$$CH_3NC \rightleftarrows CH_3CN \tag{6}$$

$$C_2H_5OCN \rightleftarrows C_2H_5NCO \tag{7}$$

$$CH_3ONO \rightleftarrows CH_3NO_2 \tag{8}$$

the nitrile (ν_{max} = 60.0). The alkyl cyanate (ν_{max} = 46) rearranges even more readily to the isocyanate (ν_{max} = 50). The nitrite (ν_{max} = 26.0) is less stable than the nitro compound (ν_{max} = 37.0).

A nice example is provided by the three isomers CH_3NO, $CH_2{=}NOH$, and $HCONH_2$. The nitrosomethane is blue (ν_{max} = 14.8) and is a transient species, rapidly forming the formaldoxime (ν_{max} = 47.0). The latter is a stable compound but in the presence of a catalyst undergoes the Beckmann rearrangement to the formamide (ν_{max} = 45.4) which must be even more stable. The Beckmann rearrangement has a complex, multistep mechanism, whereas the first reaction can occur by a simple H-atom migration.

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(11) See: Levin, C. C. *J. Am. Chem. Soc.* **1975**, *97*, 5649–5655, for a discussion.

(12) Reference 2, Vol. I, p 208.

(13) Schürgers, M.; Welge, K. H. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1968**, *23A*, 1507–1510.

(14) Strausz, O. P.; Gosavi, R. K.; Robb, M. A.; Eade, R.; Csizmadia, A. G. *Prog. Theor. Org. Chem.* **1977**, *2*, 248–260.

(15) Nagakura, S. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 164.

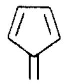
(16) Recall that the name paraffin comes from the Latin *parum affinitas*, little affinity.

The isomers of C_6H_6 give further information on the relation of spectra to stability. There are two classes of isomers, one class being the valence isomers of benzene, $(CH)_6$, such as Dewar benzene, A; prismane, B; and benzvalene, C. These can convert to the much more stable benzene by simple mechanisms, which could be concerted. The second class are structural isomers of benzene, such as fulvene, D; tris(methylene)cyclopropane, E; and bis(methylene)cyclobutene, F. These would necessarily follow complex mechanisms to convert to the more stable benzene.


A
$\nu_{max} = 48.8 \times 10^3\ cm^{-1}$


B
$\sim 48 \times 10^3\ cm^{-1}$


C
$46.1 \times 10^3\ cm^{-1}$


D
$27.8 \times 10^3\ cm^{-1}$


E
$34.7 \times 10^3\ cm^{-1}$


F
$41.7 \times 10^3\ cm^{-1}$

At first glance it is surprising that it is the valence isomers that have large values of ν_{max}, indicating stability, and the structural isomers that have low values, indicating some facile reaction. The explanation, of course, is that the valence isomers have a large activation barrier to rearrangement to benzene, imposed by orbital symmetry or other factors. The spectra are quite consistent with these barriers.

The reactivity of the structural isomers has nothing to do with their rearrangement to benzene. In fact, in the vapor state they are quite stable at temperatures of 400 °C, where they are prepared. The valence isomers become benzene at temperatures of 100 °C. The reaction to which yellow fulvene, and E and F, are unstable is a bimolecular reaction, polymerization.

The values of ν_{max} for these three molecules refer to $(\pi \rightarrow \pi^*)$ transitions. This is the same as for ethylene, butadiene, and also benzene. The excited state is a singlet diradical, though under the influences of a reagent, a zwitterion state could result.[17] Attack of a free radical on an olefin in a reaction is driven by mixing in of the $(\pi \rightarrow \pi^*)$ state.

As expected, butadiene is more reactive than ethylene toward free radicals, because of the lower value of ν_{max} (Table I). Fulvene, and E and F, would be even more reactive.[18] In the absence of other reagents, the free-radical reaction would be polymerization.

Transition-Metal Complexes. There are inorganic analogues of the linkage isomers shown in eq 6–8, except that thiocyanate ion is involved rather than cyanate. In solution, and even in the solid state, the unstable isomer rearranges to the stable one.[19] The reactions are conveniently followed by monitoring the vis–UV spectra. As expected, the first absorption band always shifts to shorter wavelengths as isomerization occurs.

The transition metals form a large number of colored complexes, most of which are quite stable in the usual sense. Fortunately the theory of the spectra of these compounds is well developed, and we can see why the low values of ν_{max} do not necessarily predict high reactivity. The very stable octahedral complexes of cobalt(III) will be used as examples.

An examination of the spectra of ions such as $Co(NH_3)_6^{3+}$, reveals the behavior shown in Figure 1b. The ligand field bands lie in the region of $(13–30) \times 10^3\ cm^{-1}$, and the charge-transfer bonds in the $(50–70) \times 10^3\ cm^{-1}$ region. The ligand field bands follow the spectrochemical series[21] of decreasing ν_{max}: $CN^- > CH_3^- > H^- >$ phen $> \mathit{N}O_2^- > \mathit{N}H_2OH > \mathit{S}O_3^{2-} >$ en $>$ pyr $\sim NH_3 > \mathit{N}H_2CH_2CO_2^- > \mathit{N}CS^- > H_2O > C_2O_4^{2-} > OH^- > (NH_2)_2C\mathit{O} > F^- > (RO)_2PS_2^- > N_3^- > \mathit{S}CN > Cl^- > Br^- > I^- \sim SO_4^{2-}$. In ambiguous cases the coordinated atom is underlined.

This order may be compared to the order of decreasing bond strengths, as given by the rates and/or equilibrium constants of the reaction:[22]

$$Co(NH_3)_5X^{2+} + H_2O = Co(NH_3)_5H_2O^{3+} + X^- \qquad (9)$$

$CH_3^- \sim H^- \sim CN^- > OH^- > \mathit{N}O_2^- > NH_3 > \mathit{N}CS^- > N_3^- \sim OAc^- \sim HC_2O_4^- \sim F^- > H_2PO_4^- \sim SO_4^{2-} \sim Cl^- > Br^- > NO_3^- > H_2O > I^-$.

There is considerable similarity between the two orders, but also many deviations. A consideration of the ligand field bands makes this intelligible. The transitions are of the $(t_{2g} \rightarrow e_g)$ variety. The t_{2g} orbitals can be n, π, or π^*, depending on whether the ligand, X^-, is non-π-bonding, a π-acceptor, such as $(C_2H_5)_3P$, or a π-donor, such as OH^-. Net π-bonding increases the bond strength and makes ν_{max} (the ligand field strength) larger. A π-donor such as OH^- causes net destabilization and makes the ligand field strength less.

This suggests that the correlation might exist, but the difficulty lies in the terminating orbital, e_g, which is a σ^* orbital for breaking the metal–ligand bond, as required. However, it is an orbital that concentrates charge on the metal atom. The corresponding $(\sigma \rightarrow \sigma^*)$ transition is a ligand-to-metal charge-transfer bond. This would be the chemically active transition for a homolytic bond cleavage.

$$Co(NH_3)_5X^{2+} + H_2O \rightarrow Co(NH_3)_5{\cdot}H_2O^{2+} + X \qquad (10)$$

To drive the heterolytic bond cleavage of reaction 9, we need to invoke metal-to-ligand charge-transfer states, which are much higher in energy. Many of the metal–ligand bonds are quite ionic, and as mentioned earlier, breaking such bonds does not require much electron reorganization. Hence dependence on excited states is small, in any case. It is not surprising that the rates of reactions such as (9) are not too well related to the spectrochemical series.

In view of the nature of the e_g orbital, a correlation between ligand field strength and rates of reduction of $Co(NH_3)_5X^{2+}$ by outer-sphere election transfer reagents might be expected. Indeed a linear relationship does exist between free energies of activation for such processes and ν_{max}.[23]

Changing the central metal ion from Co(III) to Rh(III), and then to Ir(III), causes the ligand field strengths to increase steadily, so that $Ir(NH_3)_5X^{2+}$ complexes are usually colorless. At the same time the dissociation energies for reactions analogous to (9) are increased. This is consistent with simple but unjustified expectations.

Charge-Transfer Complexes. Another well-known example of often-colored complexes are those formed between bases and weak Lewis aside, such as I_2, SO_2, $HgCl_2$, and $C_2(CN)_4$. The fact that ν_{max} is small for these systems is consistent with the small values of the bonding energies, e.g.

$$I_2 + (CH_3)_3N \quad I_2{:}N(CH_3)_3 \qquad (11)$$

$$\nu_{max} = 37.9\ kK, \Delta H = -12.1\ kcal$$

Unfortunately, it is found that there is an inverse relationship: the larger the bond energy, the smaller ν_{max}.

Again spectroscopic theory explains this discrepancy.[24] The ground state for these charge-transfer complexes is covalent, and the excited state is ionic. Clearly this excited state cannot help

$$I_2{:}N(CH_3)_3 \xrightarrow{h\nu} I_2^-{:}N(CH_3)_3^+ \qquad (12)$$

to dissociate the complex into I_2 and $(CH_3)_3N$. Again high-energy excited states that transfer electron density back from I_2 to $(CH_3)_3N$ are needed.

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(17) For a discussion of $\pi \rightarrow \pi^*$ states in olefins, see: Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.

(18) Because it is a different class of compound, benzene cannot be compared directly to the olefins.

(19) Baselo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1967; pp 291–300.

(20) Known as crystal field theory, or better as ligand field theory. See: Jorgensen, C. K. *Modern Aspects of Ligand Field Theory*; North Holland/American Elsevier, Amsterdam/New York, 1971, for example.

(21) Reference 19, p 67.

(22) Reference 19, pp 164–166.

(23) Reference 19, pp 513–515.

(24) Mulliken, R. S.; Person, W. B. *Annu. Rev. Phys. Chem.* **1962**, *13*, 107–120.

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Other reactions of the complexes do have rates that correlate with ν_{max}. In a series of examples, Fukuzumi and Kochi[25] have shown that electrophilic substitution shows a good correlation between rate constants (log k) and ν_{max} for a series of substituted benzenes and of olefins. Taking chlorination as an example, the mechanism is

$$Cl_2 + C_6H_6 \rightarrow C_6H_6{:}Cl_2 \quad (13)$$

$$C_6H_6{:}Cl_2 \xrightarrow{k} C_6H_6Cl^+, Cl^- \quad (14)$$

$$C_6H_6Cl^+, Cl^- \rightarrow C_6H_5Cl + HCl \quad (15)$$

In this case the charge-transfer transition (12) is just the one needed to drive the rate-determining step (14).

Any Lewis acid-base reaction can be considered to lead to a charge-transfer complex, with partial transfer of electrons from the base to the acid. The molecule NaBr can be considered as formed from Na^+ and Br^-. In such cases the ground state is very ionic, and the excited state is covalent. Accordingly, the

$$Na^+{:}Br^- \xrightarrow{h\nu} Na, Br \quad (16)$$

charge-transfer band is the transition that drives the reaction, since the gas-phase dissociation will be to the neutral atoms. This accounts for the good linearity shown in Figure 2.

Charge-transfer bonds are usually very intense, since they are fully allowed and have a high transition moment. Even if ν_{max} is in the UV, there can be a long tail that extends into the visible and gives rise to color. This is the case with the permanganate ion, where ν_{max} in water is actually 52.9 kK, well into the ultraviolet. The bond is a ligand-to-metal charge-transfer transition.

Summary. Even if only the first absorption band is considered, there is evidently a great deal of chemical information in the electronic spectra of molecules. However, it is usually necessary to use spectroscopic theory to identify the nature of the first band. In most cases only elementary theory is needed. It is also necessary to compare families of molecules that are closely related in some way.

A large value of ν_{max} is a reliable indication of high kinetic stability. Conversely, a colored molecule is very likely to show high reactivity,[26] but only for reactions consistent with the nature of the transition.

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(26) Especially small molecules. A large delocalized molecule might have the activating effect of the first transition widely diffused over many atoms. An example would be the dyes based on triphenylmethane.

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Recombination of $Cr(CO)_n$ with CO: Kinetics and Bond Dissociation Energies

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Abstract: The pressure dependence of the recombination kinetics of $Cr(CO)_5$ and $Cr(CO)_4$ with CO has been studied with the technique of time-resolved infrared laser absorption spectroscopy. The high pressure limiting rate constants are 2.1×10^6 and 7.5×10^6 Torr^{-1} s^{-1} for $Cr(CO)_5$ and $Cr(CO)_4$, respectively. The rate at which vibrationally excited metal carbonyls, $[Cr(CO)_n]^*$, are collisionally stabilized has been estimated: $k_s = 2.6 \times 10^5$ and 2.5×10^7 Torr^{-1} s^{-1} for collisions with He and $Cr(CO)_6$, respectively. These data, in conjunction with an RRKM model for the unimolecular decay of $Cr(CO)_6$ and $Cr(CO)_5$, allow us to determine the metal-ligand bond dissociation energies; DH°[$(CO)_5Cr$-CO] = 37 ± 5 kcal/mol and DH°[$(CO)_4Cr$-CO] = 25 ± 5 kcal/mol.

Time-resolved infrared absorption spectroscopy has recently been applied in characterizing the chemistry of a variety of organometallic species in the gas phase.[1-4] Such studies can provide useful data on dissociation dynamics, primary photochemical channels, reactive intermediate structure, and lifetimes for bimolecular reactions. Information of this type, while valuable in and of itself, is essential in developing mechanistic models for processes, e.g., homogeneous catalysis, where coordinatively unsaturated metal centers may be involved.[5] Perhaps the seemingly most simple question that can be formulated to this end is the following: How do the decomposition products of a photochemically activated organometallic reagent, $M(CO)_n^*$, depend on excitation wavelength? The answer to this question apparently depends on experimental conditions. Condensed-phase photolyses characteristically yield products derived from cleavage of a single metal-CO bond, regardless of excitation wavelength.[6] More extensive fragmentation may be observed in gas-phase experiments.[7] How do solvent molecules attenuate reactivity in this way? A priori, one might suggest that efficient collisional relaxation of vibrational and/or electronic energy may serve to (partially) quench reactivity in condensed phases relative to the gas phase. The evaluation of questions such as those posed above requires data on the photophysics, primary photochemistry, and thermochemistry (i.e., bond dissociation energies) of organo-

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