converted to internal energy in the collision process.[31] A shift of 0.1 mass unit in the CA spectrum of Figure 14 would require a kinetic energy loss of 0.9 eV. Such shifts become appreciable, however, for processes involving higher activation energies on precursor ions of higher masses (or when using lower accelerating voltages) and appear to be a valuable way to measure the average energy imparted by collision to the precursor ions yielding a particular product ion.

Applications of this technique to the determination of molecular and ion structures and to the elucidation of unimolecular ion reaction mechanisms will be discussed separately.[32] Collisional activation should be especially valuable for ions generated by chemical or field ionization which exhibit a low degree of fragmentation.

Acknowledgments. The authors acknowledge with pleasure helpful discussions with S. H. Bauer, W. A. Chupka, G. A. Fisk, I. Sakai, H. D. R. Schuddemage, T. Wachs, and B. Widom. Helpful criticisms of the referees led to important modifications of the kinetic treatment.

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Vacuum Ultraviolet Absorption Spectra of the Chloromethanes

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Abstract: The vacuum ultraviolet absorption spectra of the chloromethanes and three dichloroalkanes are given with extinction coefficients in the 50,000–90,000-cm^{-1} region. Assignments of most of the Rydberg transitions are made for methyl chloride; several of the lower energy absorptions of the chloromethanes are assigned by analogy of the spectral features. However, the higher energy absorptions cannot be assigned due to intramolecular perturbations and natural diffuseness of the spectra. Attempts to calculate the intramolecular perturbations in terms of the independent systems approach are discussed. By comparison of the oscillator strengths and band maxima for spectra of the chloromethanes, the $\sigma^* \leftarrow \sigma$ transitions are approximately located. The results are also considered in light of some recent photoelectron spectra of the same compounds. Certain analogies are readily seen, but the full relationship between the optical and photoelectron spectra is not completely understood at this time.

The investigation of the electronic spectra of several molecules which differ sequentially by one atom provides clues for assignments as well as suggesting additional molecular spectra to "test" the plausibility of specific assignments. The vacuum ultraviolet spectra of the fluoromethanes, which involve sequential substitution of fluorine into methane, have been reported and assigned in terms of the independent systems model by Edwards and Raymonda.[2] The absorption bands were assigned to the $(\sigma^* \leftarrow \sigma)_{\mathrm{C-H}}$ manifold and evidence was presented for postulating considerable Rydberg-on-hydrogen character for the basic $(\sigma^* \leftarrow \sigma)$ transition in C–H. Transitions arising from the fluorine nonbonding electrons and the $(\sigma^* \leftarrow \sigma)_{\mathrm{C-F}}$ manifold are not expected in the energy region investigated. Additional absorption bands have been reported[3] for these fluorine-substituted molecules in a higher energy region. An alternate interpretation,[4] which criticizes the independent systems model, of the fluoromethane spectra in terms of a molecular orbital description has been presented where the absorption bands were assigned as pure Rydberg transitions. That interpretation closely parallels the ideas to be presented here for the chloromethanes.

The chlorine-substituted methanes, in addition to the C–H transitions, are expected to have several absorption bands in the 50,000–90,000-cm^{-1} region arising from the nonbonding electrons and possibly the $(\sigma^* \leftarrow \sigma)_{\mathrm{C-Cl}}$ transitions.

The vuv spectra of some of the chloromethane molecules have previously been reported separately with varying degrees of experimental detail.[5,6] The spectrum of methyl chloride was initially reported in this region by Price[5] in 1936, and tentative assignments were given according to the theoretical arguments proposed by Mulliken.[7] In 1955 Zobel and Duncan[6] reported the spectra of the remaining members of this group of molecules and suggested assignments for some of the absorption bands. However, the spectra in these earlier studies were given in terms of relative intensities, and absolute oscillator strengths could not be determined.

In this paper the spectra of the four chloromethanes

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(1) (a) North Texas State University; (b) California State University; (c) University of Arizona.

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(6) C. R. Zobel and A. B. F. Duncan, *J. Amer. Chem. Soc.*, **77**, 2611 (1955).

(7) R. S. Mulliken, *Phys. Rev.*, **47**, 413 (1935); **61**, 277 (1942).

Table I. CH_3Cl Proposed Vibrational Assignments for Structures Accompanying Rydberg Transitions[a]

Vibrational assignment	S-envelope		P-envelope		D-envelope	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
ν_0^1	62,580	(62,580)	71,110	(71,110)		
ν_0^2	63,460	(63,460)	71,778	(71,778)	74,300	(74,300)
$\nu_0^1 + \nu_3^1$	63,460	63,469	~72,000	72,000		
$\nu_0^1 + \nu_2^1$	63,750	63,880	72,425	72,410		
$\nu_0^2 + \nu_3^2$	64,360	64,349	72,693	72,667	75,178	75,189
$\nu_0^1 + 2\nu_3^1$	64,360	64,358	72,693	72,888		
$\nu_0^2 + \nu_2^2$	64,770	64,760	73,088	73,078	75,607	75,600

[a] For ν_b^a, a refers to which of the Rydberg pairs the frequency is to be associated with, while b refers to the mode excited. Calculated frequencies are based on the following assumptions (Herzberg,[b] assumption): ν_2(ground) = 1355, ν_2(excited) = 1300; ν_3(ground) = 732, ν_3(excited) = 889. Values in parentheses are assumed. [b] G. Herzberg, "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945.

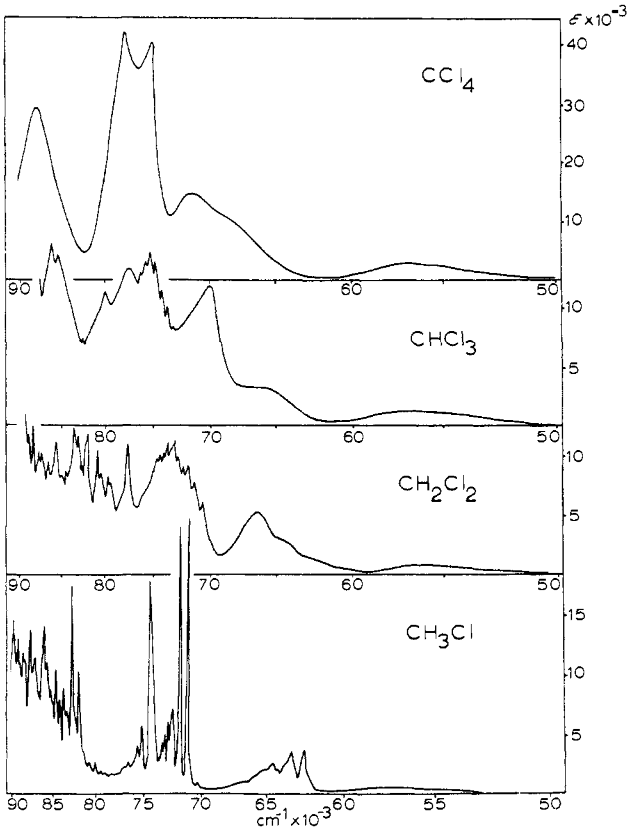

Figure 1. The vuv spectra of the chloromethanes from 50,000 to 90,000 cm^{-1}. Note that the ionization potentials are aligned to facilitate comparison of the Rydberg series transitions. Also note that the ordinate of the CCl_4 spectrum is double that of the other spectra. The abscissa is linear in wavelength; the ordinate is in units of l. $mol^{-1} cm^{-1}$.

and several dichloro-*n*-alkanes in the 50,000–92,000-cm^{-1} region are given in terms of molar extinction coefficients. Oscillator strengths for the chloromethanes are also given for absorption bands which occur in the energy region below 80,000 cm^{-1}. Recently, Lucazeau and Sandorfy[8] included the spectra of chloroform, with extinction coefficients, in a study of many aldehydes in this spectral region. The spectra of all the chloromethanes are given in Figure 1 for ease of comparison and to obtain an internally consistent set of oscillator strengths.

Assignments of Transitions from Nonbonding Levels

Methyl Chloride. Methane shows no optical absorption below 70,000 cm^{-1}, and where absorption occurs it is devoid of structure.[2] Hence, the large differences between the spectra of methane and the chlorinated methanes must be due to either the nonbonding electrons of the chlorine or the carbon–chlorine bonding electrons. The weak diffuse band in the spectrum of methyl chloride extending from 50,000 to 60,000 cm^{-1} with a maximum at 58,170 cm^{-1} is assigned as the $\sigma^* \leftarrow \sigma$ transition in accord with previous workers.[7,9] The σ^* orbital is suggested by Mulliken[7] to be localized in the C–Cl bond; the broad, diffuse contour of the band also suggests an antibonding (σ^*) orbital. The next band, centered at about 64,000 cm^{-1}, is assigned as the 4s ← n Rydberg transition. Its relative diffuseness is due to molecular involvement,[5] and it is expected that the lowest lying "Rydberg" transition should differ markedly from the atomic chlorine 4s ← 3p.

The structure of this transition may be analyzed if one assumes that there are two pairs of Rydberg series differing by about 880 cm^{-1}; each Rydberg series presumably goes to a different spin–orbit component of the ^2E ground state of the CH_3Cl^+ ion.[7] The ν_2 and ν_3 vibrational modes then appear on each Rydberg electronic transition in the same combinations as were observed for the analogous transition in methyl bromide;[10] see Table I, S-envelope.

The two intense and sharp absorption peaks at 71,070 and 71,750 cm^{-1} are assigned to the 4p ← n Rydberg transition, while the 5p ← n are weak but observable at 81,570 and 82,290 cm^{-1}. The splitting of these p states has been described by Mulliken elsewhere.[5,7] Another intense absorption peak (quantum defect = 0.35) appearing at 74,240 cm^{-1} has been tentatively assigned to the 3d ← n Rydberg. While this quantum defect is of the order of magnitude usually associated with d series, the possible assignment of 4p ← n cannot definitely be ruled out. Vibrational sequences similar to that observed on the 4s ← n system are also present on these three Rydberg transitions (see Table I). Definitive vibrational assignments are difficult because the CH_3Cl^+ spin–orbit interval and the C–Cl stretching frequency[10] are similar in magnitude and are easily confused. The spectrum of CD_3Cl would be of interest in this regard; it will be reported in the near future. A large number of peaks are observed

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(8) G. Lucazeau and C. Sandorfy, *J. Mol. Spectrosc.*, 35, 214 (1970).

(9) H. Tsubomura, K. Kimura, K. Kaya, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jap.*, 37, 417 (1964).

(10) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967, see ref 326 and pp 237 and 528.

just below the ionization potential of 90,840 cm^{-1} but not all have been assigned to Rydberg series. Consideration of the $\sigma^* \leftarrow \sigma$ intensities will follow discussion of the Rydberg states.

Methylene Chloride. The lowest energy electronic absorption is observed in the 50,000–60,000-cm^{-1} region for CH_2Cl_2 and has been assigned[9] as the $\sigma^* \leftarrow \sigma$. The second absorption band extends from *ca.* 60,000 to 70,000 cm^{-1} with the band maximum at 66,270 cm^{-1} with a shoulder at 64,350 cm^{-1}. It is believed that this whole area is the result of the two degenerate 4s ← n transitions, one on each of the chlorine atoms. Justification (other than location) is that the intensity is approximately double (actually ~2.5; see Table II) that of the corresponding region in CH_3Cl, and one might predict that the interactions of the isolated 4s ← n Rydberg transitions would be small and not cause great intensity redistribution. The shape of the band is in good agreement with an independent systems type calculation,[11] using the transverse polarization of the 4s ← n in CH_3Cl as the reference vector. Useful predictions have been obtained elsewhere[2,11,12] using an independent systems approach where the interacting transitions were polarized parallel to the bond direction. In those cases, the size of the interaction was approximated by a dipole interaction using the transition dipoles classically. Such a dipole approximation was tried for this transverse case but the predicted magnitude of the splitting was far too small (about 20%) to fit the observed spectra. However, the intensity pattern, that is, with the higher energy member having about 70% of the intensity, is in unexpectedly good agreement with the spectra.

Table II. Absorption Maxima[a] and Oscillator Strengths

Assignment	CH_3Cl	CH_2Cl_2	$CHCl_3$	Cl_4
$\sigma^* \leftarrow n$	58.1	56.8	57.2	56.8
f values	0.02	0.05	0.09	0.11
4s ← n	64.0	66.4	70.0	71.4
f values	0.16	0.40	1.10	1.30
4p, 3d ← n[b]	71.1	73.2	75.4	77.4
f values	0.40	1.67	2.10	3.45

[a] The absorption maxima in energy units of 1000 cm^{-1}. [b] This absorption has underlying intensity from $\sigma^* \leftarrow \sigma$ absorptions (see text).

In an effort to understand the failure of the transition dipole approximation to predict the magnitude of the splitting, the spectra of 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane were taken (see Figure 2). In these molecules the separation of the chlorine atoms is much greater, and the interaction should be considerably reduced. However, we found in all three cases that the shapes and intensities of the corresponding peaks (4s ← n) were nearly identical! The nature of the interaction appears to be distance independent, and therefore may not even be a chlorine–chlorine type interaction. Thus, although the successful prediction of the intensity distribution pattern using the transversely polarized dipole interaction approximation was at first encouraging, the concomitant failure of the approach to predict the magnitude of the splitting in methylene chloride and to predict the lack of change in the spectra of the more extended dichlorides, ruled out further use of the theory (at this time) in the interpretation of this band.[13]

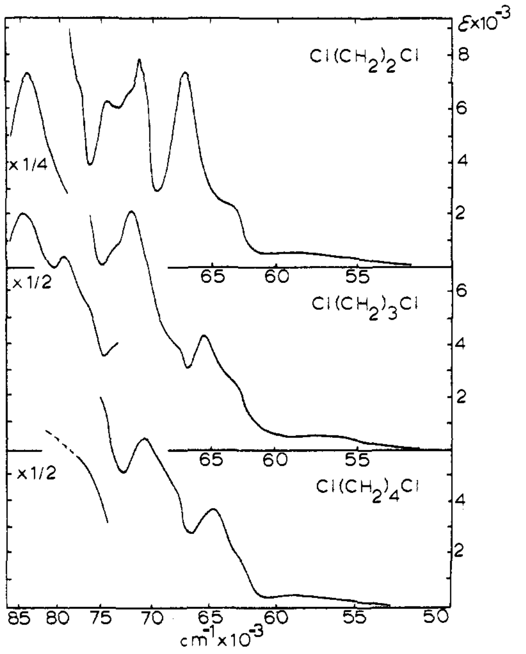

Figure 2. The vuv spectra of 1,2-dichloroethane, 1,3-dichloropropane, and 1,4-dichlorobutane in the 50,000–85,000-cm^{-1} region. The intensities, especially in the region above 75,000 cm^{-1}, are accurate to ±20%. Note that the splitting of the peak and shoulder in the 60,000–66,000-cm^{-1} region remains approximately constant as the separation of the chlorine atoms changes. The abscissa is linear in wavelength; the ordinate is in units of l. mol^{-1} cm^{-1}.

The third absorption band begins at 69,250 cm^{-1} and extends at 76,600 cm^{-1} with a maximum at 72,940 cm^{-1}. The vibrational structure of this band has been tentatively assigned by Zobel and Duncan[6] as corresponding to C–Cl stretching and H–C–H bending. This band is centered about where the 4p ← n is expected to occur based on the assignment in CH_3Cl, and at least part of the intensity (and all the structure) is believed due to the nearly degenerate 4p ← n transitions. Beginning with a fairly sharp band at 77,280 cm^{-1}, a series of about 15 Rydberg-like (*e.g.*, see CH_3Cl) peaks are observed, but no successful assignment scheme was found based on the Rydberg formula.

Chloroform. The initial electronic absorption occurs in the 50,000–60,000-cm^{-1} region and has been assigned[9] as the $\sigma^* \leftarrow \sigma$ transition, with the band maximum from this work at 57,210 cm^{-1}. This band is obviously related to the $\sigma^* \leftarrow \sigma$ transitions of CH_3Cl and CH_2Cl_2. The oscillator strength is 0.09, and seems high compared with expectations based on CH_3Cl and CH_2Cl (see Table II).

The shoulder at 66,000 cm^{-1} has only about the same intensity as both the peak and shoulder in CH_3Cl in the corresponding region and cannot reasonably be assigned as possessing all the 4p ← n intensity. The proximity and intensity of the higher absorptions, in addition to making accurate band shapes undeterminable, may also lend considerable intensity to the region

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(11) J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, **47**, 430 (1967).

(12) R. H. Partridge, *ibid.*, **49**, 3656 (1968).

(13) An alternative idea is that the splitting observed is between the in-plane and out-of-plane chlorine 3p orbitals in the ground state due to the low symmetry of the higher dichlorides. We are grateful to the referee for this suggestion.

up to 70,000 cm^{-1}. Because of these intensity considerations and the overall band shape (similar to CH_3Cl), the peak at about 70,000 cm^{-1} and the shoulder at about 66,000 cm^{-1} are both believed to stem from the 4p ← n manifold. Higher energy absorptions appear complex, consisting of several bands, the first having some vibrational structure. Still higher energy regions above *ca.* 80,000 cm^{-1} contain a notably smaller number of Rydberg-like peaks than are present in CH_3Cl or CH_2Cl_2. The one dominant feature is a doublet at 85,180 and 85,940 cm^{-1}, ϵ_{max} 15,000 l. mol^{-1} cm^{-1}.

Carbon Tetrachloride. The absorption assigned[9] as the $\sigma^* \leftarrow$ n begins at *ca.* 50,000 cm^{-1} and extends to 60,000 cm^{-1} with the maximum from this work at 56,790 cm^{-1}. A second distinct region begins at *ca.* 60,000 cm^{-1} and extends to 73,400 cm^{-1} with a maximum at 71,480 cm^{-1}. The unsymmetrical shape of this region is suggestive of two bands; indeed, there appears to be a shoulder at *ca.* 69,400 cm^{-1}. Once again the shape of the peak and its shoulder, the overall intensity (f = 1.30), and approximate location imply that the source of intensity for this region is related to the degenerate 4p ← n transitions.

The third distinct absorption is the extremely intense (ϵ_{max} 40,000 l. mol^{-1} cm^{-1}) doublet at 75,400 and 76,900 cm^{-1}. The spectrum of carbon tetrachloride has certain similarities to the spectra of several other tetrachlorides[14] in the region above *ca.* 60,000 cm^{-1}. Five tetrachlorides studied thus far have a "doublet" type absorption in the 77,000-cm^{-1} region with the principal distinction among the various spectra being in the intensity of this band; implication is that the spectral structure seems related to the chlorides and the tetrahedral geometry. It should also be noted that the splitting of the doublet in CCl_4 is nearly identical to the splitting of the 4p ← n and 3d ← n Rydbergs in CH_3Cl and perhaps is attributal to those Rydberg components.

Additional features of note below the ionization potential (92,500 cm^{-1}) are a very deep valley (ϵ 4000 l. mol^{-1} cm^{-1}) at about 84,000 cm^{-1} and a relatively sharp, intense peak at 88,950 cm^{-1} which may be related to the high energy doublet in chloroform. No Rydberg-like peaks are resolved.

Consideration of $\sigma^* \leftarrow \sigma$ Transitions

Recent photoelectron spectra of the chloromethane molecules[15-17] indicate that the nonbonding electrons are about 2.5 to 4.0 eV (1 eV = 8067 cm^{-1}) less tightly bound that the bonding (σ) electrons; thus, one would expect to see the effects of σ electrons below 90,000 cm^{-1}. The $\sigma^* \leftarrow \sigma$ transitions are not expected to show sharp structure, but rather, because the σ^* orbital is primarily antibonding, they are nearly always quite diffuse and broad. When they appear in consort with Rydberg structure, they usually manifest themselves only as background intensity, occasionally lending strength to Rydberg transitions. The intensity in the valley at about 78,000 cm^{-1} in CH_3Cl is less than the methane intensity at this frequency, and seems to indicate that little background intensity is present. Indeed, since all the features below 78,000 cm^{-1} can be accounted for by nonbonding electrons, it is believed that no $\sigma^* \leftarrow \sigma$ transitions are contributing to the absorption in this lower energy region of CH_3Cl.

One of the outstanding features of the CCl_4 spectrum is the great intensity in the 77,000-cm^{-1} area; ϵ 40,000 l. mol^{-1} cm^{-1}. This is far more than simply four times the intensity of the same region in CH_3Cl, and its source must be other than the nonbonding electrons. Much of the intensity in this region of CCl_4 is probably due to the $\sigma^* \leftarrow \sigma$, C–Cl transitions. Before proceeding further, one must properly take into account the degeneracy of these transitions.

For strong transitions polarized along the bond (parallel), the independent systems approach has been useful.[2,11,12] For the degenerate manifold, that theory predicts that most of the $\sigma^* \leftarrow \sigma$, C–Cl intensity will be split down (shifted to lower energy) by the (dipole) interaction. In CH_3Cl, the lone $\sigma^* \leftarrow \sigma$, C–Cl is not degenerate and will not shift down. In CH_2Cl_2, $CHCl_3$, and CCl_4, the $\sigma^* \leftarrow \sigma$, C–Cl intensity should come at the same frequency.

Although the Rydberg transitions may interact to some extent, their total intensity is expected to be conserved, and any new intensity introduced into the lower energy regions as one proceeds through the series of molecules must come from other sources.[18] If we now consider the total intensity below the "natural" valley always near 78,000 to 80,000 cm^{-1} (thereby taking into account the intensity of the n to σ^*, 4s, 4p, 3d), we find an anomalous increase with progressive chlorine substitution, which is assigned as originating from $\sigma^* \leftarrow \sigma$, C–Cl transitions. The independent systems predictions for the amount of this increase, which are based on group theoretical arguments at this point, are in very good agreement with the data. While exact predictions of band positions are not expected, semiquantitative results should be reliable, and it appears that the region between 75,000 and 80,000 cm^{-1} grows abnormally large in intensity as chlorine atoms replace hydrogen atoms in the series (see Table II). Thus, it is believed that the original $\sigma \rightarrow \sigma^*$, C–Cl intensity in CH_3Cl (unsplit) lies above 80,000 cm^{-1}, and due to interactions among the degenerate $\sigma \rightarrow \sigma^*$ transitions, most of the C–Cl intensity is shifted down to about 77,000 cm^{-1} in the higher chlorine substituted methanes; this presumably is the source of the great intensity at 77,000 cm^{-1} in CCl_4. Again, these transitions are to antibonding orbitals and are expected to be diffuse and broad; therefore they are not believed to be contributing to the sharp structure observed in most of the spectra, but rather to be providing relatively large amounts of underlying intensity.

The $\sigma \rightarrow \sigma^*$ of C–H is relatively much less intense and contributions from these cannot be discerned. In CH_3Cl at least, they are believed to contribute to the region above 78,000 cm^{-1}.

Further Discussion

Although several theoretical approaches were considered to correlate the data, no consistently applicable results were obtainable. At times, calculations with CNDO/2 programs and at other times calculations with the independent systems approach showed promise,

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(15) R. N. Dixon, J. N.Murrell, and B. Narayan, *Mol. Phys.*, **20**, 611 (1971).

(16) M. B. Robin and N. A. Kuebler, private communication.

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but when applied to all the data, all self-consistent approaches had definite shortcomings. Undoubtedly, the exact interplay of all the Rydberg structure and the various intensity patterns is complex.

There is currently additional interest in the photoelectron spectra of these compounds.[15–17] Sometimes useful correlations can be discerned when one compares the photoelectron and optical spectra. Certain major intensity correlations can be naively drawn between the two sets of data and may suggest sources of intensity. For example, in the optical spectrum of CCl_4, one sees basically three large groups of intensity (disregarding the weaker first transition). The centers of these intensity groups are separated by roughly 7 kK, with the middle member being the most intense and showing doublet structure. The photoelectron spectrum shows the same structural pattern, again with the separations of the three major intensity groups being about 7 kK and the middle member showing some structure. Also, in $CHCl_3$, the major intensity pattern of the photoelectron data is again three major bands of intensity with the middle being most intense. This pattern is repeated in the optical spectrum of $CHCl_3$. While no one-to-one correspondence is intended, it is suggested that transitions involving electrons other than just the highest filled orbital electrons may be playing a part in the overall intensity distribution in the optical spectra. For example, it seems certain that the σ electrons in the C–Cl bond must be considered. More work needs to be done before such correlations are understood, and efforts are being made in those directions.

Acknowledgments. The authors thank W. T. Simpson for his helpful suggestions concerning transverse moments during the early phases of this work. B. R. R. would like to acknowledge financial support of faculty research from North Texas State University and the Robert A. Welch Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (J. W. R.). We are grateful to the referee for several helpful suggestions.

Ambident Behavior of Nitrite Ion. Reactions of 2,4-Dinitrohalobenzenes and 1,2,4-Trinitrobenzene with Sodium Nitrite[1]

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Received January 29, 1972

Abstract: The reaction of sodium nitrite in aqueous acetonitrile (3:2) at pH 7 and 25° with the four 2,4-dinitrohalobenzenes clearly demonstrates the ambident nature of the nitrite ion. The relative importance of the two modes of displacement, O attack and N attack, depends on the halogen displaced, oxygen attack increasing with increasing electronegativity of the halogen. Dinitrofluorobenzene reacts totally by O attack, whereas dinitroiodobenzene reacts altogether by N attack. Dinitrochloro- and dinitrobromobenzene demonstrate both modes of displacement. The rates of oxygen and nitrogen attack by nitrite ion were determined for each of the 2,4-dinitrohalobenzenes, and the rate of oxygen attack was determined for 1,2,4-trinitrobenzene.

Nitrite ion has two potential reaction sites.[2] In 1955, Kornblum[3] coined the term "ambident anions" to describe species having multiple reaction sites. Gompper[4] preferred to speak of "ambifunctional nucleophilic compounds." The ambident nature of nitrite ion in organic metal complexes is well documented.[5] Complexes with both nitro and nitrito linkages are known, some having both linkages in the same complex. The type of bond appears to be dependent on the electronic structure of the metal and the steric requirements imposed by other ligands. Evidence exists for nitro–nitrito equilibria in some complexes,[5] and a number of nitro-coordinated compounds are prepared from their nitrito isomers that have formed initially as unstable intermediates.

Also well documented[3] is the nitrite ion reaction with alkyl halides to give a mixture of alkyl nitrites and nitroalkanes. The relative amounts of these products, resulting from oxygen and nitrogen attack, respectively, depend on many factors: cation, halide, solvent, temperature, and alkyl structure. The reaction of silver nitrite with para-substituted benzyl bromides showed that *p*-methoxybenzyl bromide gives a greater ratio of nitrite ester to nitro compound than does *p*-nitrobenzyl bromide. Kornblum concluded that the greater the carbonium ion like character of the halogen compound in the transition state, the more likely the nitrite ion is to attack through the oxygen atom. With the strongly positive center of a carbonium ion like species, the reaction is controlled by electrostatic attraction to the more electronegative oxygen atoms. When

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