Vacuum Ultraviolet Absorption Spectra of Some Chloroalkanes

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Abstract: The electronic absorption spectra of several alkyl chlorides in the energy region of 50,000 to 90,000 cm^{-1} are presented with extinction coefficients. Oscillator strengths for all major distinct areas of intensities were calculated. These oscillator strengths were used to aid in the correlation of the absorption bands arising from the nonbonding electrons of chlorine to aid in spectral assignments. In addition, an oscillator strength sum rule is demonstrated for these transitions, and, as a result of deviations from this empirical rule, a higher energy absorption in the spectrum of *n*-butyl chloride is attributed to a $\sigma^* \leftarrow \sigma$ transition in that compound. With full consideration and comparison of the spectra of the alkyl chlorides to the spectrum of methyl chloride, many assignments are made. The absorption band at 74,240 cm^{-1} in the spectrum of methyl chloride has been reconsidered and is assigned as the first member of a Rydberg series leading to the second ionization potential.

The electronic absorption spectra of methyl chloride and other alkyl chlorides have been studied previously by Price,[2,3] but only preliminary assignments were offered; graphs of absorption intensity *vs.* energy were not shown. Price found a pair of Rydberg series with quantum defect about 0.5 leading to the two lowest energy states of the CH_3Cl^+ ion, $^2E_{1/2}$ and $^2E_{3/2}$. Mulliken[4] later considered the hydrogen and alkyl halide spectra and developed an assignment scheme for a number of bands which has not been improved. This scheme is applied to methyl chloride in Table I and is taken as the basis for further assignments in the alkyl chlorides. The spectrum of methyl chloride is shown in Figure 1 to aid the reader in using Table I.

We have reexamined the spectra of methyl chloride and other alkyl halides as well and present the spectra here with reliable intensities. We point out some correlations of excited state term values among the several spectra which serve to locate the Rydberg transitions in this series of molecules. Location of Rydberg-related transitions then facilitates identification of valence shell transitions.[5]

Experimental Section

The spectra were recorded on several spectrographs, both photoelectrically and photographically, always in the vapor phase. The instruments and techniques have been described elsewhere.[6-8] Spectra from the various spectrographs always agreed to within ±10 cm^{-1} on positions of sharp bands, ±50 cm^{-1} on positions of broad band maxima, and ±15% on absolute intensities.

All materials are readily available in sufficient purity (greater than 99%). Liquids were outgassed by several freeze–thaw cycles before being admitted to the sample chamber. Gases were used directly from the lecture bottles.

Discussion

The spectra of several alkyl chlorides are shown in Figure 2. The oscillator strengths of the first few absorption bands in each compound are tabulated in Table II. Bands were resolved as objectively as possible. The errors in the oscillator strengths are estimated conservatively at ±15%. *n*-Butyl chloride tended to adsorb on surfaces, rendering pressure measurements somewhat uncertain. The intensity of that spectrum may be too low by as much as 50%; this error of course propagates directly to the oscillator strengths. We first discuss methyl chloride briefly with reference to Table I and Figure 1; this discussion is a continuation and extension of ideas presented in an earlier paper.[9]

Methyl Chloride. The weak diffuse band extending from 55,000 to 60,000 cm^{-1} is assigned as an $\sigma^* \leftarrow n$ transition, according to Mulliken's intensity considerations.[10] The σ^* orbital is localized in the C–Cl bond; Mulliken has suggested that it might have 3dσ (Cl) character.[4]

The next band, centered at about 64,000 cm^{-1}, is probably best described as 4s ← n where the 4s type orbital is largely localized on the chlorine but may also contain some admixture of carbon and hydrogen orbitals. The splitting of the peaks at 62,570 and 63,470 cm^{-1} is due to spin–orbit interaction in the core, as discussed by Mulliken.[4] The remaining bands are not well resolved, and a definitive analysis in terms of vibronic progressions is not readily achieved. Tentative assignments have been presented in our previous work.[9] The overall diffuseness of this transition is thought to be due to strong predissociation. The postulated excited state has the same symmetry as the nearby $\sigma^* \leftarrow n$ state, and perhaps a single configuration description of these states is not appropriate due to mixing of the configurations. This could enhance the predissociative nature of the 4s ← n state.

Price[2] and Mulliken[4] both considered the sharp, intense pair of bands at 71,070 and 71,750 cm^{-1} but ignored the equally intense band at 74,240 cm^{-1}. This pair constitutes the first members of Price's Rydberg series with a quantum defect of 0.5. Mulliken[4] assigned these as 4p ← n transitions, parallel bands, on the basis of barely resolved doublet structure in the bands on Price's photographic plates. We have been unable to find any such doubling on a 2.217-m spectro-

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[2] W. C. Price, *J. Chem. Phys.*, **4,** 539 (1936).

[3] W. C. Price, *J. Chem. Phys.*, 4, 547 (1936).

[4] R. S. Mulliken, *Phys. Rev.*, **61,** 277 (1942).

[5] L. B. Clark and W. T. Simpson, *J. Chem. Phys.*, **43,** 3666 (1965).

[6] J. W. Raymonda, Ph.D. Dissertation, University of Washington, 1966.

[7] L. O. Edwards, Ph.D. Dissertation, University of Oregon, 1969.

[8] J. D. Scott and B. R. Russell, *J. Amer. Chem. Soc.*, **94,** 2634 (1972).

[9] B. R. Russell, L. O. Edwards, and J. W. Raymonda, *J. Amer. Chem. Soc.*, **95,** 2129 (1973).

[10] R. S. Mulliken, *J. Chem. Phys.*, **8,** 382 (1940).

Table I. Assignments in Methyl Chloride[a]

Band description Label[b]	Energy[c]	Intensity	Type	Assignment	Excited configuration	Approximate MO's
A	55 to 60	Weak	Continuum	$\sigma^*_{\mathrm{C-Cl}} \leftarrow \mathrm{n_{Cl}}$	$(\sigma a_1)^2(\pi e)^3(\sigma^* a_1)^1\ {}^3E, {}^1E$	$\sigma = a(3p\sigma_{Cl}) + b(\sigma_{Me})$ $\pi = 3p\pi_{Cl}$ $\sigma^* = c(\sigma_{Me}) - d(3p\sigma_{Cl})$
B	62.57	Medium	Diffuse	$4s_{Cl} \leftarrow n_{Cl}$	$(\sigma^2\pi^3, {}^2\Pi_{3/2})b\sigma$	$b\sigma = 4s_{Cl}$
C	63.47	Medium	Diffuse	$4s_{Cl} \leftarrow n_{Cl}$	$(\sigma^2\pi^3, {}^2\Pi_{1/2})b\sigma$	Others as above
D	71.07	Strong	Sharp	$4p_{Cl} \leftarrow n_{Cl}$	$(\sigma^2\pi^3, {}^2\Pi_{3/2})c\pi$	$c\pi = 4p\pi_{Cl}$
E	71.75	Strong	Sharp	$4p_{Cl} \leftarrow n_{Cl}$	$(\sigma^2\pi^3, {}^2\Pi_{1/2})c\pi$	Others as above

[a] Based upon ref 3. Assignments of lowest energy transitions in methyl chloride according to Mulliken. [b] Price's labels,[2] used later by Mulliken.[4] [c] Energies in cm^{-1} × 10^3.

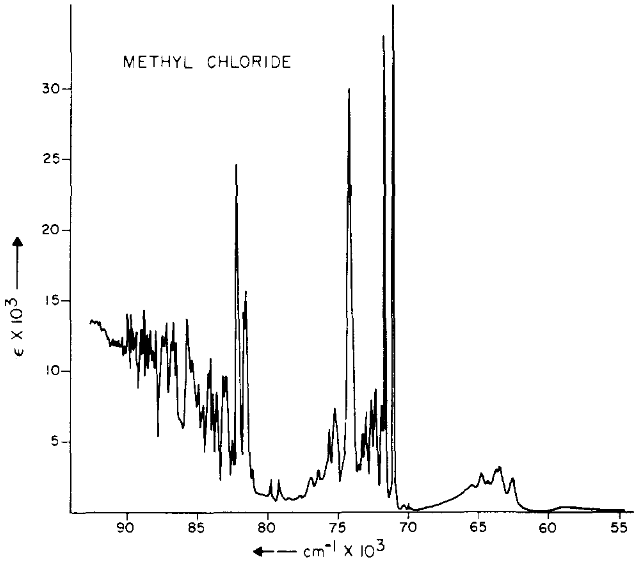

Figure 1. Spectrum of methyl chloride. Energy is in cm^{-1} × 10^3. Intensity is in l./(cm mol).

Table II. Oscillator Strengths for Alkyl Chloride Rydberg Transitions

Compd	$\sigma^* \leftarrow$ n	4s $\leftarrow$ n	4p $\leftarrow$ n	Total
Methyl	E^a 58	64	74	
	f^b 0.02	0.16	0.30	0.48
Ethyl	E 58	64	71.5	
	f 0.02	0.23	0.42	0.67
n-Propyl	E 58	63.5	69	
	f 0.02	0.16	0.42	0.60
Isopropyl	E 58	63	68	
	f 0.015	0.24	0.28	0.56
n-Butyl	E 58	63.5	*d*	
	f 0.015	0.16	*d*	
1,2-Dichloro	E 58	65[c]	73	
	f 0.05	0.425	0.83	1.31

[a] Energies in cm^{-1} × 10^3. See Figure 2. Labeling is according to the band maximum or the apparent center of the Franck–Condon envelope, whichever is appropriate. [b] $f = 1.3 \times 10^{-8} \int \epsilon d\bar{\nu}$, $\bar{\nu}$ in cm^{-1}, ϵ in l./(cm mol). [c] Assignment uncertain. Oscillator strength for the whole system over the 62–68 range given. See text. [d] Unable to resolve a definite band. No oscillator strength measured.

graph operated at a resolution of at least 0.1 Å. Nevertheless, we accept the assignment as a 4p ← n transition because of the reasonable size of the quantum defect. Further members of this series were found by Price[2] and by us, the most prominent of which are the 5p ← n pair at 81,570 and 82,290 cm^{-1}.

Mulliken[4] stated that neither d-type Rydberg series nor higher members of the s series could be found in the methyl chloride spectrum. Such an observation is puzzling, as Mulliken pointed out, since d ← p and s ← p series would be strong in the chlorine atom and p ← p transitions would be forbidden, while the opposite seems to be true of the chlorine atom in methyl chloride. The spectrum of methyl chloride was searched for evidence of s- and d-Rydberg transitions, with high expectations as a result of technical improvements in the instrumentation; however, we were unsuccessful in finding d ← p Rydberg transitions.[11,12] Thus, a weak

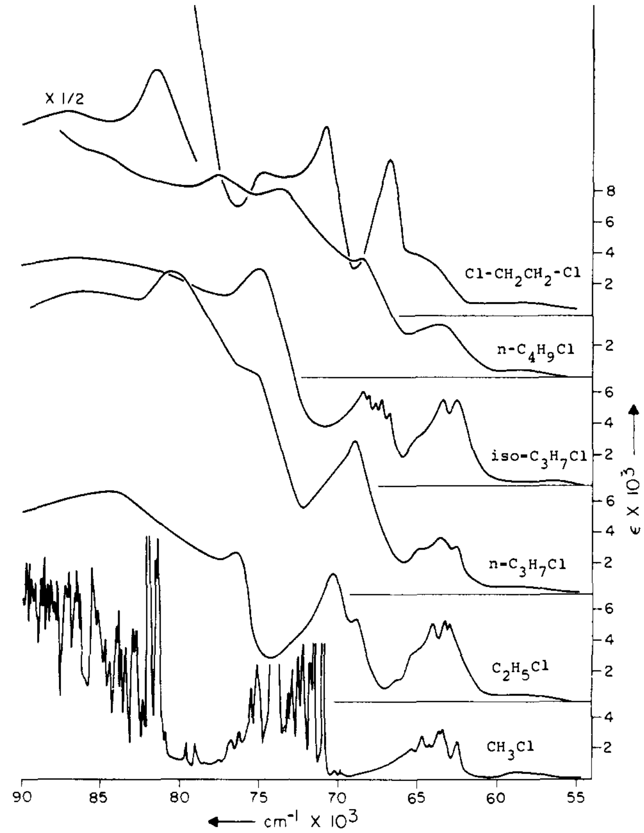

Figure 2. Spectra of several alkyl chlorides. The spectrum of methyl chloride is shown here with its tallest band cut short to avoid overlapping with the spectra above it. Methyl chloride is shown in full in Figure 1. Energy is in cm^{-1} × 10^3. Intensity is in l./(cm mol). Intensity scales are all equal except as noted.

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(11) It should be noted, in connection with this, that d-type transitions with quantum number *n* and quantum defect ~0.01 to 0.1 might be hard to distinguish from s-type transitions with quantum number *n* + 2 and quantum defect δ ~1.9 to 2.0, especially at high *n*. However, the s-Rydberg transitions come in simple pairs split by the spin-orbit coupling interval characteristic of the core, while d-Rydberg manifolds could be considerably more complex owing to the three azimuthal types of d orbitals, transitions to all of which are allowed in C_{3v} symmetry. On the basis of both the simplicity of the band systems

pair of bands with separation characteristic of the spin–orbit splitting in other first ionization potential Rydberg states of methyl chloride is found at 79,180 and 79,830 cm^{-1}. These are assigned as 5s ← n split by spin–orbit interaction in the core, since they fit into a Rydberg series with quantum defect δ 1.90. Higher members of this series can also be found, but we do not discuss them here.

We now turn to the strong band at 74,240 cm^{-1}. This band was shown by Price in his schematic representation of the methyl chloride spectrum[2] but was not discussed by him; Mulliken also did not treat it.[4] Initially, we considered the d ← n assignment for this absorption but ultimately rejected this idea; see ref 12. Instead, we prefer to assign this transition as the 0–0 band of the first Rydberg transition of a series leading to the second ionization potential of methyl chloride for reasons we now discuss.

The location of the 0–0 transition of the second ionization of methyl chloride is approximately 13.9 eV or 112,000 cm^{-1}.[17] This yields an effective quantum number n^* ($= n - \delta$) for the 74,240-cm^{-1} band of 1.7. Tilford and his coworkers have discovered very strong 0^+ ($^1\Sigma^+$) bands in HI (at 68,277 cm^{-1}) and HBr (at 79,646 cm^{-1}) which have effective quantum numbers of 1.59 and 1.60, respectively, relative to the second ionization limits.[16] These limits involve placing the ion in a $^2\Sigma^+$ state, and the resulting 0^+ Rydberg bands are thus single since the core has no spin–orbit coupling. The second ionization in methyl chloride involves loss of an electron from the molecular orbital which is mainly responsible for C–Cl bonding,[18] and the resulting ion is thus in a state of A_1 symmetry (C_{3v} group). Rydberg transitions leading to the second ionization will therefore be single owing to lack of spin–orbit coupling in the core. Thus the analogy between the 74,240-cm^{-1} band of methyl chloride and the 68,277- and 79,646-cm^{-1} bands of HI and HBr is clear and can be taken as support[19] of our chosen assignment.

We now turn to the correlation of many prominent bands of the higher alkyl chlorides with transitions of methyl chloride.

Higher Alkyl Halides. Each alkyl chloride (Figure 2) has a weak band in the 55,000 to 60,000 cm^{-1} region with contour closely resembling the 55,000 to 60,000 cm^{-1} band of methyl chloride. These bands are all of comparable oscillator strength (f) except in 1,2-dichloroethane where the f is about double that of the monochlorides. It is reasonable to suppose that the model, involving a localized σ^* orbital adopted by Mulliken[10] to explain the 55,000 to 60,000 cm^{-1} band in methyl chloride, is applicable in the higher chlorides as well. We therefore assign these bands as $\sigma^* \leftarrow$ n transitions with the concomitant assumption that the σ^* orbital is strongly localized in the C–Cl region of the molecule.

Similarly, each monochloride has a band extending over the 61,000 to 67,000 cm^{-1} region and with oscillator strength comparable to the 4s ← n transition in methyl chloride. It seems reasonable to associate these bands with 4s ← n transitions in the higher chlorides. We note that as the structure of the alkyl fragment varies these bands do *not* shift in energy "following" the ionization potential, despite their other apparent Rydberg (4s) characteristics. We suggest, in agreement with Price,[2,3] that this is evidence for considerable valence shell character for the excited orbital involved in this transition. The excited electron must be localized in the vicinity of the C–Cl moiety since the position and intensity of the transition is relatively insensitive to the structure of the alkyl group bearing the chlorine atom.

1,2-Dichloroethane deserves special mention. The absorption extending from 62,000 to 69,000 cm^{-1} has an oscillator strength about double those of the 4s ← n bands of the monochlorides (Table II), suggesting that the whole absorption belongs to 4s ← n transitions, since now we have two chlorines in the molecule.

The photoelectron spectrum of 1,2-dichloroethane (shown in Figure 3) shows two resolved ionization potentials (IP) split by 3700 cm^{-1}. However, there are actually four linear combinations of 3px and 3py orbitals from the two chlorines, and four IP's rather closely spaced, corresponding to these orbitals, are expected. Since the envelope of the lower IP is so much broader than that of the higher one, it is possible that several IP's are present there. Scans of the spectrum at higher resolution did not resolve the first band any further, however. We therefore suppose that the Rydberg transitions leading to these IP's will also come in pairs, but the splittings may be somewhat different since now there are several linear combinations of excited orbitals to consider as well.

With the above in mind, we now return to considera-

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at 79,180 and 79,830 cm^{-1} and our confidence that the quantum defect is slightly less than 2 and not slightly more than 2, we strongly prefer the 5s ← n assignment for these transitions.

(12) In view of recent work on the spectrum of atomic chlorine[13-15] in which the states arising from the configuration 3s^2 3p^4 (3p) 3d have been found to have a term value very similar to that of the 74,240-cm^{-1} band of methyl chloride (14,500 cm^{-1} in atomic chlorine *vs.* 16,600 cm^{-1} in methyl chloride), it is tempting to assign the 74,240 cm^{-1} as a 3d ← n Rydberg. However, as mentioned in the previous reference, such a Rydberg would be expected to display a rather complex structure; in particular, the 650-cm^{-1} interval characteristic of the CH$_3$Cl$^+$ core spin–orbit coupling should be discernible. Instead, the 74,240-cm^{-1} system appears to consist of a prominent single 0–0 band followed by a number of weaker bands signifying vibrational excitation of the electronic excited state. We tentatively adopted the d-Rydberg assignment in our previous work[9] because it seemed the strongest of the alternatives then available to us, the new information[16] (see text) from Tilford's laboratory not having been known to us at that time.

(13) C. J. Humphries and E. Paul, Jr., *J. Opt. Soc. Amer.*, **49**, 1186 (1959).

(14) L. Minnhagen, *J. Opt. Soc. Amer.*, **51**, 298 (1961).

(15) A. R. Striganov and N. S. Sventitskii, "Tables of Spectral Lines of Neutral and Ionized Atoms," Plenum Press, New York, N. Y., 1968, p 298.

(16) S. G. Tilford, private communication.

(17) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, p 224. The energy of the adiabatic (0–0) IP was estimated from the given photoelectron spectrum.

(18) Unpublished CNDO/2 calculations by the authors.

(19) It should be noted that the assignments by Tilford of the bands in HI and HBr to 0^+ states are on a firm basis since they result from analyses of resolved rotational structure. This is especially important with regard to these bands in HI and HBr since they consist of strong 0–0 bands which might otherwise be mistaken for transitions arising from promotions of nonbonding electrons, rather than bonding electrons, as is actually the case. Similarly, the 74,240-cm^{-1} band in methyl chloride resembles a transition of the n (nonbonding) → R (nonbonding) type, and a rotational analysis of a resolved high resolution spectrum of the band would be the best basis for a definitive assignment. However, this is not feasible at the present time for experimental reasons, and it is unlikely that it will ever be possible in any case, judging from the extent to which all the excited states of methyl chloride seem to be predissociated. It is therefore felt that the apparent strong analogies between the 74,240-cm^{-1} band in methyl chloride and the above mentioned firmly assigned bands in HI and HBr form the best available basis for an assignment of the 74,240-cm^{-1} transition. It is, admittedly, difficult to understand why transitions apparently involving bonding electrons should appear so vertical in any of the molecules under consideration here.

Table III. Correlation of Rydberg States in Alkyl Chlorides[a]

Assignment in methyl chloride	Term value in methyl chloride[b]	Term values[c] of observed transitions in higher alkyl chlorides				
		Ethyl	*n*-Propyl	Isopropyl	*n*-Butyl	1,2-Dichloroethane
n → 4p	19.4 (71.4)	19.5 (69.1)	18.4 (69.0)	19.5 (67.3)	17.6 (68.4)	21.2 (70.7) 20.1 (74.5)
n → 5s	11.5 (79.3)	12.0 (76.6)	11.6 (75.8)	11.8 (75.0)	12.4 (73.6)	10.4 14.5 (81.5)[d]
n → 5p	9.4 (81.4)	Obsd	Obsd	Obsd	8.8 (77.2)	10.4 (81.5)[d] 8.6 (87.0)
IP's[c]	90.5 91.2 Av = 90.8	88.6	87.4	86.8	86.0	1st = 91.9 2nd = 95.6

[a] All energies in cm^{-1} × 10^3. [Term values given with regard to the average of the ionization potentials leading to the two states, $^2\Pi_{3/2}$, $^2\Pi_{1/2}$, of the CH_3Cl^+ ion. [c] Term values are measured with respect to the ionization potentials shown in the bottom line of the table. Quantities in parentheses are the absolute energies of the spectral features to which the assignment refers. IP's of methyl chloride are from ref 2 and those of 1,2-dichloroethane are from the photoelectron spectrum recorded by one of the authors (J. W. R.) while the guest of Dr. M. B. Robin and Bell Telephone Laboratories. See the Appendix for the full spectrum. Other IP's are from K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962), and are spectroscopic IP's because a self-consistent set of vertical IP's for all the compounds could not be found. [d] Most probably all the n → 5s and n → 5p transitions are included under the very intense broad features at 81500 and 87000 cm^{-1} in 1,2-dichloroethane.

tion of the 62,000 to 69,000 cm^{-1} band system of 1,2-dichloroethane. The system appears to be two bands, not quite resolved but separated by about 2500 cm^{-1}. This splitting is close to that appearing in the photoelectron spectrum, and it is thus very tempting to assign the whole system as 4s ← n transitions. However, when it is recalled, from above, that the 4s ← n transitions do not "follow" the IP's in the monochlorides, then it is not obvious that the splitting of the IP's in the dichloride should be at all reflected in a splitting of the 4s ← n transitions since such a splitting is tantamount to "following." Theory is not much help in resolving this question. The shape of the band system, with the bulk of the intensity in the blue region, is in harmony with the predictions of independent systems (IS) theory.[6,7,20] In the IS picture, electrons are localized in both ground and excited states, conceivably a reasonable model for 4s ← n transitions on the separate chlorine atoms. However, the IS splitting, which is calculated as the electrostatic interaction between transition densities at the chlorines using experimental intensities to obtain numerical predictions, is much smaller than the observed splitting. Thus it is apparent that the through space interactions of the IS model cannot alone account for the observations. On the other hand, molecular orbital (MO) theory, which pictures all electrons as delocalized in principle, is not sufficiently reliable to be applied to the interpretation of this band system. Taking only 3p*x*, 3p*y*, and 4s orbitals on each chlorine as the basis set, eight excited singlet configurations are obtained whose relative energies and intensities are sensitive functions of parameters which can neither be calculated accurately nor reliably chosen for a semiempirical scheme. Moreover, the importance of configuration interaction is hard to assess. Therefore, we cannot say with confidence at this time that the entire 62,000 to 67,000 cm^{-1} band system should be assigned to 4s ← n excitations. There seems little doubt, however, that at least part of it, most likely the low energy part, should be assigned as 4s ← n because of the strong analogy of this part, with apparent center at about 64,000 cm^{-1}, to the monochlorides. The taller band at 66,700 cm^{-1} might then have a different source, but we do not suggest one in this work.

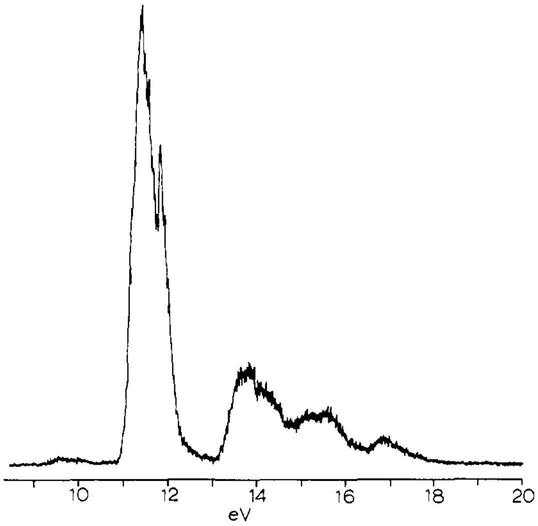

Figure 3. Low-resolution photoelectron spectrum of 1,2-dichloroethane. The vertical scale is proportional to counts per second of photoejected electrons.

The 4p ← n, 5p ← n, and 5s ← n Rydbergs of methyl chloride are found to have analogs which do follow the IP's in the higher chlorides. That is, a number of bands can be found with term values equal or nearly equal to the term values for these Rydberg states in methyl chloride. The results are summarized in Table III.

It is seen that in most cases, definite peaks can be found for all but the 5p ← n transition, which is distinguishable only in *n*-butyl chloride and 1,2-dichloroethane. Note also that 4p ← n transitions correlating with both observed IP's in 1,2-dichloroethane can be found.

As a final point, we call attention to an interesting sum rule, apparently obeyed by the first few transitions of all the chlorides shown in Figure 2 except *n*-butyl chloride. Notice first that each spectrum has a well-defined valley at which one might choose to partition the absorption. These occur at 78,500 cm^{-1} in methyl chloride, 74,500 cm^{-1} in ethyl chloride, 72,000 cm^{-1} in *n*-propyl chloride, 71,000 cm^{-1} in isopropyl chloride, and

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(20) E. G. McRae and M. Kasha, "Physical Processes in Radiation Biology," Academic Press, New York, N. Y., 1964, pp 23-42.

76,500 in 1,1-dichloroethane. No such valley can be found in *n*-butyl chloride and we therefore omit it temporarily from this discussion. In methyl chloride, the absorption below the valley includes the $\sigma^* \leftarrow \mathrm{n}$, $4\mathrm{s} \leftarrow \mathrm{n}$, and $4\mathrm{p} \leftarrow \mathrm{n}$ transitions; similarly, these same transitions are all found below the valley in the other chlorides we are considering. It is well known that the total oscillator strength of the absorptions arising from transitions of a given pair of electrons should equal 2. If we assume that the distribution of the oscillator strength among the various possible transitions originating from the n electrons is the same in all these chlorides, we are led to expect an analogous sum rule to hold for a given group of transitions, such as those listed above.

Let us now consult Table II in which the measured oscillator strengths are set down. For methyl chloride we show the oscillator strength for only that part of the 70,000 to 78,500 cm^{-1} region which we have assigned to $4\mathrm{p} \leftarrow \mathrm{n}$ transitions; the $\mathrm{R} \leftarrow \sigma_{(\mathrm{C-Cl})}$ Rydberg has been subtracted out. However, in the higher chlorides we have not found analogs to this transition; therefore, the oscillator strengths shown for these chlorides include all the intensity below the valley even though $\mathrm{R} \leftarrow \sigma$ Rydbergs could be present there. In spite of this, we see that the total oscillator strength below the valley is approximately a constant for the monochlorides (excluding *n*-butyl) and is about twice as great for the dichloride. This suggests that the bulk of the intensity below the valleys in all these compounds has a common source, the n electrons.

Valence Shell Transitions. The preceding discussion suggests that all the intensity below the valley in the chlorides is Rydberg in origin. Since the magnitude of this intensity is roughly constant and since the valence shell ($\sigma^* \leftarrow \sigma$) transitions are reasonably intense ($f \geqq 0.2$),[21] it would appear that the $\sigma^* \leftarrow \sigma$ transition involving the C–C, C–H, and C–Cl bonds occurs (only) above the valley. In *n*-butyl chloride, the apparent absence of a valley is taken as evidence that the lowest energy $\sigma^* \leftarrow \sigma$ transition has come down low enough to obscure the valley. We may estimate the expected position of the valley in *n*-butyl chloride at about 71,000 cm^{-1}, from consideration of the trend followed by the valleys in the other chlorides. Thus the absorption attributed to the $\sigma^* \leftarrow \sigma$ transition appears to be large at this same energy in *n*-butyl chloride. As the alkyl fragment becomes larger, the $\sigma \rightarrow \sigma^*$ assigned absorption is expected to resemble more the alkane spectra; the approximate position of 71,000 cm^{-1} is in reasonable agreement with the first peak in butane, 70,500 cm^{-1}.[21]

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Appendix

The photoelectron spectrum of 1,2-dichloroethane was recorded on a photoelectron spectrometer having an electrostatic deflection analyzer and capable of resolution of at least 0.08 eV (65 cm^{-1}). A low-resolution scan taken with He(I) excitation is shown in Figure 3. Scans at higher resolution did not reveal any vibrational structure on any of the IP's. A He(II) spectrum was not recorded. The measured IP's are presented in Table IV along with our assignments; correlations with the IP's in methyl chloride are also shown. We now discuss the spectrum briefly.

Table IV. Ionization Potentials of 1,2-Dichloroethane

±0.03 eV	±250 cm^{-1}	Assignment	Corresponding IP in CH$_3$Cl[a]
11.39	91,880	3pπ	11.3
11.85	95,590	3pπ	11.7
13.75	110,920	C–Cl and C–C σ	14.4, σa_1 (C–Cl)
14.17	114,310	Skeleton	
15.09	121,730	C–H	15.3 π_e (C–H)
15.59	125,760	C–H	15.8 π_e (C–H)
16.89	136,250		

[a] Vertical IP's are quoted in eV. IP's and assignments are from ref 17, pp 224 and 240.

The weak signals at 10 eV are part of the spectrometer background. No IP's belonging to 1,2-dichloroethane and lower than 11 eV were found. The 11–12-eV region contains two partially resolved peaks of unequal intensity. This whole region is assigned as containing the four IP's expected from the four possible linear combinations of 3px and 3py on the two chlorines.

The second IP in methyl chloride corresponds to removal of a C–Cl bond electron.[16] In 1,2-dichloroethane, the electrons of the C–C bond and the two C–Cl bonds can be considered localized in the neutral ground state, but the hole resulting from removal of one of these electrons is delocalized over all the bonds. Therefore, three distinct IP's can be expected, probably all in the same region as the second IP of methyl chloride. It seems reasonable to assign the 13–14.5-eV bands to these IP's. It is obvious from the band contour that at least two IP's are located there.

Similarly, the 15–16-eV bands are assigned to C–H orbitals, again by correlating with methyl chloride.

The band at 16.9 eV has no analog in methyl chloride and we do not assign it here.

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