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Temporary negative ions in the chloromethanes CHCl_2F and CCl_2F_2 : Characterization of the σ^* orbitals

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Temporary negative ions in the chloromethanes CHCl_2F and CCl_2F_2 : Characterization of the σ^* orbitals

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In this work, electron transmission spectroscopy (ETS)¹ is employed to study low-lying temporary anions in the chloromethanes. The resulting electron affinities (E.A.), within the context of Koopmans' theorem, may be associated with the energies of the low-lying unfilled orbitals of these compounds. Such data are of fundamental importance for an understanding of the electronic structure of molecules, and are relevant to studies of fragment anion production by electron capture through the dissociative attachment mechanism, to the interpretation of optical absorption spectra of the neutral molecules, and to electron impact studies of inner-shell electron excitation.

ETS has proven to be a sensitive technique for the study of short-lived anion states formed by capture of electrons into the normally unfilled π^* orbitals of unsaturated hydrocarbons.^{2,3} However, such measurements in small saturated hydrocarbons have been less useful, because the anion states associated with the antibonding orbitals in these systems lie at high energies and have very short lifetimes, and hence, broad widths. In recent work, however, we found that chlorine substitution on ethylene⁴ and benzene⁵ produced additional features in the transmission spectra other than those due to the π^* orbitals. We have attributed these to the filling of low-lying C-Cl σ^* orbitals. In support of this assignment, we expect that similar anion states should exist in the chlorinated alkanes, and in this note we describe our results in the simplest molecules of this class.

In Fig. 1, we present the transmission spectra of the chloromethanes, CHCl_2F , and CCl_2F_2 , plotting the derivative of the unscattered electron current transmitted through the gas cell as a function of electron impact energy.⁶ The vertical arrows below the curves are at the observed midpoints between dip and peak and

correspond to the vertical attachment energies, i.e., the negative of the vertical electron affinities.⁷

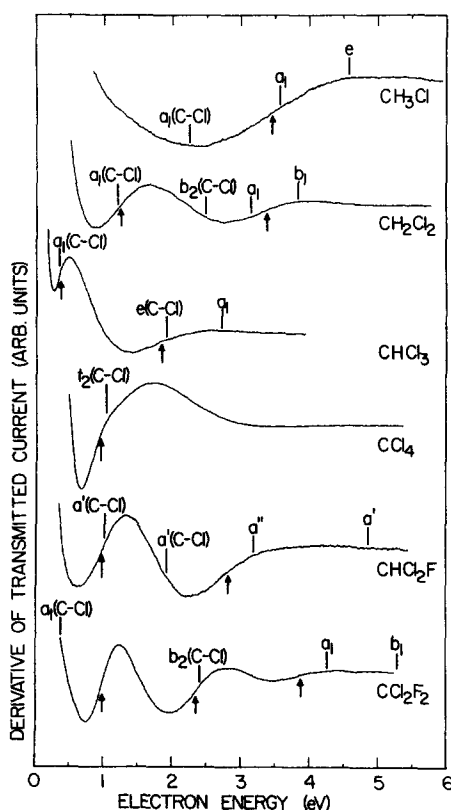


FIG. 1. Derivative of transmitted current as a function of electron impact energy. The vertical arrows beneath the curves locate the vertical attachment energies. The lines above each curve indicate the theoretical anion energies and orbital symmetries. The theoretical energies are normalized to the experimental data only at the 2A_1 resonance in CHCl_3 .

TABLE I. Vertical electron affinities (eV).^a

CH ₃ Cl	-3.45	
CH ₂ Cl ₂	-1.23, -3.38	
CHCl ₃	-0.35, -1.83	
CCl ₄	>0, -0.94	
CHFCl ₂	-0.96, -2.81	
CF ₂ Cl ₂	-0.98, -2.35, -3.88	

^aThe midpoints of the structures may be located to within ± 0.04 eV. The association of these energies with the E.A.'s will be less certain for the broader resonances.

The numbers and relative positions of the anion states shown in Fig. 1 are fully consistent with a simple picture in which there is one low-lying anion state associated with each C-Cl bond. Keeping in mind the degeneracies connected with the various molecular symmetries, as well as the experimental evidence that the 2A_1 ground state anion of CCl₄ is stable⁸ and thus inaccessible to ETS, we expect a single anion state of 2A_1 symmetry to appear in CH₃Cl and a triply degenerate 2T_2 anion in CCl₄. Two anion states associated with C-Cl σ^* orbitals are expected for both CHCl₃ and CH₂Cl₂, of 2A_1 and 2E symmetry in the former, and 2A_1 and 2B_2 in the latter. The E.A.'s determined from ETS are summarized in Table I.

To support these assignments we have carried out *ab initio* SCF calculations on the neutral molecules at their experimental geometries⁹ using the Gaussian 70 program¹⁰ and 4-31G basis sets. A set of relative electron affinities is obtained from the negatives of the energies of the unoccupied orbitals. These were normalized to the experimental data by addition of 3.37 eV, crudely accounting for basis set deficiencies and reorganization effects, bringing the first theoretical E.A. of CHCl₃ into agreement with the experimental value for this compound. This feature was chosen as the reference since it corresponds to the narrowest feature observed in the chloromethanes. The theoretical energies thus obtained are shown by dashed vertical lines in Fig. 1. The orbitals which are predominantly C-Cl σ^* in character are so indicated.

For the chloromethanes the agreement between the predicted and measured E.A.'s is good for the anion states below 2.5 eV. For the two highest lying anion states, the agreement is less satisfactory. In CH₂Cl₂, the second anion lies 0.9 eV above the calculated position of the 2B_2 state. Although a calculated 2A_1 state lies closer, the association appears less likely since the unoccupied a_1 orbital has little charge density in the C-Cl bond. We note that the low-level calculations used here are likely to be least appropriate for high-lying short-lived anion states.

In the fluorine compounds the theoretical calculations again locate the C-Cl σ^* orbitals well below the C-F σ^*

and C-H σ^* orbitals, although the relative spacings are not quantitatively given at this level of calculation. Fluorine substitution is observed to stabilize the C-Cl σ^* orbitals, and in CCl₂F₂ causes a third anion state at 3.88 eV which is predominantly C-F σ^* in nature.

Previous discussions of the electronic spectra of these compounds have not taken into account the large splittings in the σ^* orbitals we observe with ETS. The n (lone pair) - C-Cl σ^* transitions, e.g., are generally assumed to fall close together forming the broad "A" band.¹¹ We note here the possibility that in CH₂Cl₂ through CCl₄, the bands above A may contain a second $n - \sigma^*$ transition, possibly the so-called "X" or undesignated band.¹² This suggestion is supported by optical absorption measurements¹³ in CCl₂F₂ which indicate, according to the interpretation of Robin,¹¹ two A bands spaced by 1.3 eV, in excellent agreement with the spacing between the lower σ^* orbitals observed here using ETS.

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COMMENTS

Third and fourth virial coefficients of hard hyperspheres of arbitrary dimensionality

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Luban and Baram have calculated the third and fourth pressure virial coefficients of hard hyperspheres of arbitrary dimensionality 2ν .¹ These coefficients can be related to the following integrals:

$$\begin{aligned}\mu_\nu &= \int_0^\infty dx x^{-(\nu+1)} [J_\nu(x)]^3, \\ g_\nu(y) &= \int_0^\infty dx x^{-\nu} [J_\nu(x)]^2 J_{\nu-1}(xy), \\ f_\nu &= \int_0^\infty dx x^{-(2\nu+1)} [J_\nu(x)]^4.\end{aligned}\quad (1)$$

Much of Ref. 1 is concerned with the details of the evaluation of these integrals, which Luban and Baram accomplish by contour integration (μ_ν and f_ν) or by applying Neumann's formula² ($g_\nu(y)$). The calculations leading to their results (A9) and (B15) are particularly tedious.

We wish to point out that all the above integrals may be evaluated very quickly and easily using the well-known formula of Sonine and Gegenbauer³:

$$\int_0^\pi d\phi \frac{J_\nu(\tilde{\omega}x)}{\tilde{\omega}^\nu} \sin^{2\nu} \phi = 2^\nu \Gamma(\frac{1}{2}) \Gamma(\nu + \frac{1}{2}) \frac{[J_\nu(x)]^2}{x^\nu}. \quad (2)$$

Here $\tilde{\omega} = 2 \sin \frac{1}{2} \phi$. To calculate μ_ν and $g_\nu(y)$ one simply uses this integral representation of $[J_\nu(x)]^2$ in Eq. (1) and then reverses the order of integration over x and ϕ (which is certainly permissible for $\nu > 0$). Noting that⁴

$$\int_0^\infty dx \frac{J_\nu(ax) J_\nu(bx)}{x} = \begin{cases} \frac{1}{2\nu} (a/b)^\nu, & a < b \\ \frac{1}{2\nu} (b/a)^\nu, & a > b \end{cases}, \quad (3)$$

and⁵

$$\int_0^\infty dx J_{\nu-1}(ax) J_\nu(bx) = \begin{cases} a^{\nu-1}/b^\nu, & a < b \\ \frac{1}{2a}, & a = b \\ 0, & a > b \end{cases}, \quad (4)$$

one finds

$$\begin{aligned}\mu_\nu &= \frac{(\frac{1}{2})^\nu (1/2\nu)}{\Gamma(\nu + \frac{1}{2}) \Gamma(\frac{1}{2})} \left(\int_0^{\pi/3} d\phi \sin^{2\nu} \phi \right. \\ &\quad \left. + \int_{\pi/3}^\pi d\phi \cos^{2\nu} \frac{1}{2} \phi \right),\end{aligned}\quad (5)$$

$$g_\nu(y) = \begin{cases} \frac{(\frac{1}{2})^\nu y^{\nu-1}}{\Gamma(\nu + \frac{1}{2}) \Gamma(\frac{1}{2})} \int_{2 \arcsin^{-1}(1/2)y}^\pi d\phi \cos^{2\nu} \frac{1}{2} \phi, & y < 2 \\ 0, & y \geq 2 \end{cases}\quad (6)$$

The remaining integrations in Eqs. (5) and (6) are trivial. The integrals may be written as incomplete beta functions,⁶ and if desired may be expressed in the forms obtained by Luban and Baram using Eq. (6.6.8) of Ref. 6.

The advantages of this method become particularly apparent when we consider f_ν . Simply applying Eq. (2) twice, and again using Eq. (3),

$$f_\nu = \frac{(\frac{1}{2})^{2\nu} (1/2\nu)}{[\Gamma(\nu + \frac{1}{2}) \Gamma(\frac{1}{2})]^2} \int_0^\pi \int_0^\pi d\phi_1 d\phi_2 (\cos \frac{1}{2} \phi_> \sin \phi_>)^{2\nu}, \quad (7)$$

where $\phi_< = \min(\phi_1, \phi_2)$ and $\phi_> = \max(\phi_1, \phi_2)$. From this result, Eq. (B15) of Ref. 1 is trivially obtained. Alternatively, in the case $\nu = N$, an integer, we may perform the standard integrations directly to obtain the following closed-form result for the virial coefficient $B_4(\square)$, in $2N$ dimensions:

$$\begin{aligned}\frac{B_4(\square)}{(B_2)^3} &= -3 + \frac{3}{\pi^2} \sum_{n=1}^N \frac{1}{n} \frac{(2n-2)!!}{(2n-1)!!} \\ &\quad \times \left[4 + \frac{2^{2n} n! N(2N)!!}{(N+n)_{n+1} (2N-1)!!} \right].\end{aligned}\quad (8)$$

Luban and Baram unsuccessfully sought such a result for general values of N (Appendix B of Ref. 1).

Therefore, for $N = 1, 2, 3$, and 4 :