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A spectroscopic study of the ground states of CHCl_2^+ and CDCl_2^+ using a new multichannel detector photoelectron spectrometer

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Although photoelectron spectroscopy is widely used to study stable molecules, special techniques are required to obtain well-resolved photoelectron spectra (pes) of transient species to provide vibrational data on the ground state cation. Fluorine atom abstraction reactions have proved a useful source of free radicals for pes studies,¹⁻⁵ but contamination in the ionization chamber limits the time available for recording spectra under the most sensitive conditions. Consequently, a minicomputer operated multichannel detector photoelectron spectrometer has been developed in this laboratory to decrease data acquisition time for transient species. Several halomethyl cations have been isolated in solid argon using matrix photoionization methods, and their most intense infrared absorptions have been recorded.⁶⁻¹⁰ Recently, secondary photolysis has increased the yield of CHCl_2^+ in solid argon, and the weaker symmetric C-Cl₂ stretching mode was observed at 845 cm⁻¹.¹¹ We report here the first photoelectron band of CHCl_2^+ which contains a vibrational progression in the latter mode for CHCl_2^+ with a $\nu' = 0-1$ separation of 860 ± 30 cm⁻¹.

Dichloromethyl radicals were produced in the photoionization chamber of the spectrometer by the reaction of fluorine atoms with CH_2Cl_2 (May and Baker, Ltd.) and CD_2Cl_2 (Aldrich, 99.6% D) in a discharge flow system. The radicals were ionized by He(I) radiation. Photoelectron spectra were recorded over the 8.0-18.0 eV ionization energy region to monitor the reaction as a function of reagent mixing distance and over the 8.2-10.4 eV range with CH_3I added to calibrate¹² the new structured product band.

The method used for generating transient species resulted in considerable contamination of the reaction region; initial experiments performed on a photoelectron spectrometer used for previous transient work⁴ gave an

unstructured band for the radical species. Later experiments employed a new spectrometer with a rapid data collection system and sample differential pumping in the ionization region. The essential elements of the detection system were a channel plate/phosphor screen/SIT camera assembly which replaced the conventional single detector (channeltron) system and allowed for considerable reduction of data collection time. In addition the two-dimensional image could be monitored and optimized throughout the course of the run. Photoelectron intensity data were collected over the 8.2-8.8 eV region at the rate of 250 scans per 5 s and corrected for transmission of the multidetector plate and phosphor screen assembly using a LSI-11 minicomputer and a unique dedicated, dual-buffer data interface; this cycle was repeated for successive energy windows. Sample differential pumping in the ionization region was achieved by restricting the reactants and products to a sample chamber within the main ionization chamber of the spectrometer and using the ionization chamber diffusion pump to act as the source of differential pumping. This modification reduced the contamination of the electron optical components and permitted an extension of species observation time. Consequently, spectra could be recorded rapidly to minimize spectral drift problems, and repeated over 2-3 h periods to confirm results. Full details of this apparatus will be described elsewhere.¹³

Photoelectron spectra recorded using reagent mixing 1 cm above the photon beam revealed unreacted F atoms, unreacted CH_2Cl_2 (about half of that introduced), the first band of HF with components at 16.06 and 16.41 eV and a structured product band in the region 8.2-9.0 eV ionization energy. Other bands associated with Cl atoms and HCl secondary reaction products were observed.⁵ At longer mixing distances with the same re-

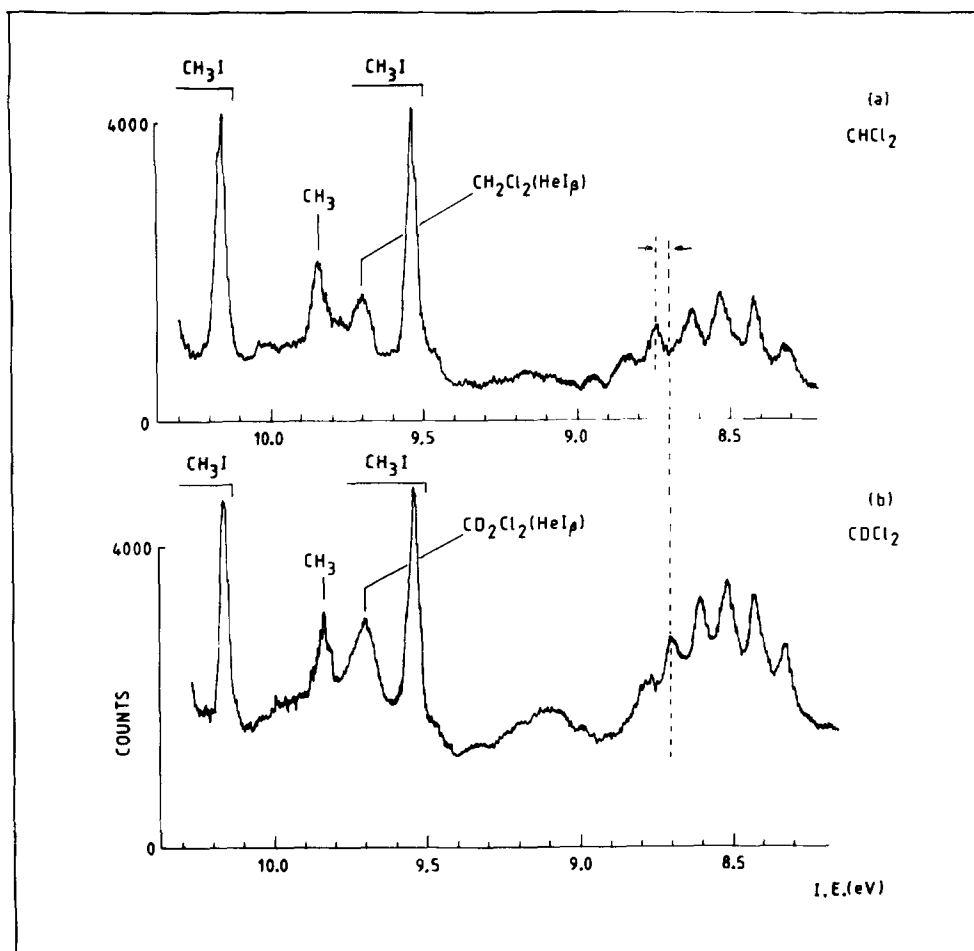


FIG. 1. He(I) photoelectron spectra recorded on a multi-channel detector spectrometer in the 8.2–10.4 eV ionization energy region for the primary product of the fluorine atom-methylene chloride reaction using 1.5 cm reagent mixing above the photon beam. (a) CHCl_2 , (b) CDCl_2 . The broad 9.0–9.2 eV I.P. band contains contributions from the first band of the precursor recorded with HeI γ radiation as well as a contribution from a secondary reaction product species.

agent partial pressures, the product band in the region 8.2–9.0 eV decreased in intensity and the HCl and Cl signals increased. The 8.2–10.4 eV region was scanned repeatedly over a 2 h period; Fig. 1(a) illustrates the addition of four sets of 1000 scans each recorded in a total time of 60 s showing the structured product band and CH_3I calibrant. The adiabatic ionization energy (8.32 ± 0.01 eV) and the vertical ionization energy (8.54 ± 0.01 eV) of this product band measured using CH_3I bracket the best available electron impact value (8.45 ± 0.05 eV)¹⁴ for the CHCl_2 radical. This agreement, the fact that this band decreases in intensity for longer mixing distances, and the higher first ionization energy of CCl_2 (9.8 ± 0.1 eV)¹⁵ support assignment of the structured product band to ionization of CHCl_2 . The isotopic shift to be described below for CDCl_2 confirms this assignment.

The $v'=0-1$ ionic vibrational separation in the CHCl_2 pes band was measured as 860 ± 30 cm^{-1} . This vibrational interval is in agreement, within experimental error, with the sharp 845 cm^{-1} CHCl_2^+ argon matrix absorption which exhibited a chlorine isotopic triplet and the proper C-13 shift for assignment to ν_2 , the symmetric C- Cl_2 stretching vibration.¹¹ The separations for each vibronic component in the structured pes band shown in Fig. 1 yield the vibrational constants $w_2 = 890 \pm 30$ cm^{-1} and $w_2 x_2 = 15 \pm 5$ cm^{-1} . This is consistent with ionization of an essentially planar radical¹⁶ to a planar

cation where the major change is in the carbon-chlorine bond length.

The spectrum recorded under identical conditions on the same evening using the CD_2Cl_2 reagent revealed DF at 16.07 and 16.33 ± 0.01 eV,¹⁷ Cl, HCl, and a slightly different structured band, which is illustrated in Fig. 1(b) for four added sets of 2500 scans. The adiabatic and vertical ionization energies (8.33 ± 0.01 and 8.52 ± 0.01 eV, respectively) exhibited small isotopic shifts. As expected, this isotopic shift becomes more pronounced at higher vibrational levels in the cations as can be seen for the fifth component at 8.74 ± 0.01 eV in the CHCl_2 and 8.70 ± 0.01 eV in the CDCl_2 spectra. The 0–1 vibrational separation in CDCl_2^+ was measured as 790 ± 30 cm^{-1} , and the vibrational intervals in the CDCl_2 spectrum give vibrational constants $w_2 = 820 \pm 30$ cm^{-1} and $w_2 x_2 = 15 \pm 5$ cm^{-1} . The deuterium shift in the ν_2 fundamental of CDCl_2^+ is due to interaction with the C–D stretching mode which has been observed for CHCl_2^+ at 3033 cm^{-1} in solid argon.¹¹

The increase in C–Cl stretching fundamentals for CHCl_2^+ as compared to the neutral species, confirmed by the present pes study, is due to increased net C–Cl bonding in the carbocation. This is consistent with the antibonding character of the outermost molecular orbital in CHCl_2 (X^2A') obtained from an *ab initio* SCF calculation. The CHCl_2^+ carbocation exhibits appreciably

stronger C-Cl bonding than the isoelectronic neutral species BHCl_2 based on the two chlorine stretching modes for $^{12}\text{CHCl}_2$ (1045, 845 cm^{-1})¹¹ and $^{11}\text{BHCl}_2$ (886, 740 cm^{-1}).^{18,19} It appears that halomethyl cations are stabilized by considerable charge delocalization.

The new multichannel detector spectrometer enables photoelectron spectra to be recorded quickly with maximum spectrometer sensitivity and minimum drift due to charge accumulation. This allows adding successive sets of scans to give an increase in signal to noise. Such capability is necessary to measure and calibrate vibronic photoelectron spectra with sufficient accuracy to determine small isotopic shifts.

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COMMENTS

About the numerical solution of the Percus-Yevick equation in the critical region for nontruncated potentials

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In a recent paper¹ we presented the results of a numerical solution of the Percus-Yevick (PY) equation near the critical point for a Lennard-Jones (LJ) fluid. According to those results, the PY equation exhibited a purely classical critical behavior, i.e., we obtained classical values for the critical exponents and the symmetry relations for the critical amplitudes.

In Ref. 1, the Fourier transforms were carried out² by substituting the upper limit ∞ by a cutoff distance R and considering N points in the interval $(0, R)$. Furthermore, in order to take into account the infinite range of the LJ potential, we assumed the asymptotic behavior $-u(r)/k_B T$ for $c(r)$. Obviously, the greater R and N are, the more accurate the method is. In Ref. 1 we took $R = 5\sigma$ and $N = 200$. These values seemed to be good enough, but the results we present here leave some doubts about them.

We have solved the PY equation for several pairs of values (R, N) using the method described in Ref. 1.

The results for some of these pairs are presented in Fig. 1, where $\ln[\gamma h(r)]$ and $h(r)$ are plotted vs r for $T = 1.3195 \epsilon/k_B$ and $\rho = 0.225\sigma^{-3}$. In the $h(r)$ plot one hardly may see a significant difference between the curves corresponding to $R = 5\sigma$ and $R = 30\sigma$. However, the influence of a finite cutoff distance R is dramatically clear in the representation of $\ln[\gamma h(r)]$. Thus, we observe in Fig. 1, a nonphysical, abrupt decay of $h(r)$ near R , which is caused by the numerical method [see Eq. (2.10) and the relations following it in Ref. 1]. But the error introduced by the method seems to affect even the small distances, especially in the cases $R = 5\sigma$ and $R = 10\sigma$. On the other hand, we have checked that, for a given value of R , an increase of N does not ameliorate the results substantially.

Figure 1 also shows a linear behavior of $\ln[\gamma h(r)]$ from $r \approx 4\sigma$ to the neighborhood of R . By extrapolation to the exact solution ($R \rightarrow \infty, R/N \rightarrow 0$), we can confirm the expected Ornstein-Zernike form for the asymptotic behavior of the net correlation function in the critical