COMMUNICATIONS

Determination of absolute photoionization cross sections for vinyl and propargyl radicals

Jason C. Robinson, Niels E. Sveum, and Daniel M. Neumark
*Department of Chemistry, University of California, Berkeley, California 94720
and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Photofragment translational spectroscopy experiments employing tunable vacuum ultraviolet photoionization yielded absolute photoionization cross sections for vinyl and propargyl radicals at 10 eV of 11.1 ± 2.2 and 8.3 ± 1.6 Mb, respectively. From these values, the photoionization efficiency curves from 7.8–10.8 eV for these radicals were placed on an absolute scale. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1606440]

The development of intense vacuum ultraviolet (VUV) light sources, including synchrotrons and VUV lasers, has led to their increasing use in chemical dynamics experiments. Photodissociation and bimolecular scattering experiments have been conducted in which the scattered products are ionized with tunable VUV radiation,[1–5] rather than by electron impact; the VUV ionization experiments result in greatly reduced fragmentation of the products, enabling the study of more complex systems than was otherwise possible. Photoionization (PI) mass spectrometry has recently been implemented as a flame diagnostic technique, in which the chemical constituents of a flame can be monitored as a function of distance from the burner.[6] However, in order for these experiments to be more quantitative, so that, for example, one can use VUV photoionization to determine product branching ratios in scattering experiments, absolute photoionization cross sections are required for the chemical species of interest.

Absolute photoionization cross sections have been measured for several closed-shell atoms and molecules,[7,8] and they have been calculated[9–11] and measured[12–16] for a few open-shell atoms, but almost no data exist for the open-shell, polyatomic radicals that are often produced in scattering experiments or flames. In this Communication, we describe the first results from what we believe to be a general method for determining absolute photoionization cross sections of polyatomic radicals. We perform a photodissociation experiment, photofragment translational spectroscopy (PTS), in which the scattered photoproducts are photoionized with VUV radiation. By comparing signal levels for momentum-matched products, we obtain the absolute photoionization cross section for one photofragment if that for the other is known. We use this method to obtain cross sections for vinyl (C_2H_3) and propargyl (C_3H_3) radicals via photodissociation of C_2H_3Cl and C_3H_3Cl, respectively, at 193 nm, making use of the photoionization cross sections for Cl reported by Ruscic[13] and others.[8,14–16]

Vinyl chloride has been studied previously at 193 nm using PTS coupled with tunable VUV synchrotron radiation to determine primary and secondary decomposition channels.[17] The 193 nm light excites a $\pi^* \leftarrow \pi$ transition in vinyl chloride. Blank *et al.* found that excited vinyl chloride decays to produce a chlorine atom and a vinyl radical through two primary processes, with one process occurring on an excited state surface and the other following internal conversion to the ground state surface. The excited state process was found to be dominant, with an observed anisotropy parameter of $\beta = +1.1$. Similarly, propargyl chloride has been studied using PTS coupled with electron impact detection.[18] The initially prepared (π, π^*) state is predissociated by a (n, σ^*) state. Atomic chlorine loss was found to produce the propargyl radical with an observed $\beta = +0.2$.

Our method for determining cross sections of radicals bears some similarity to recent studies by Flesch *et al.*[16,19] In their work, the photoionization cross section of ClO was determined by UV photodissociation of OClO and Cl_2O, followed by VUV photoionization and mass-spectrometric detection of all reactants and products in the interaction region. The ClO cross section was extracted by comparison of ClO^+ and either the Cl^+ or O^+ signal levels, using the known PI cross section for Cl or O at a particular VUV wavelength. The PTS/VUV experiment differs in that it focuses on scattered photoproducts and, as shown below, can be applied even in the presence of secondary dissociation processes or large velocity mismatches between the two photofragments. It should therefore be applicable to more complex systems where such effects are expected.

The experiments described in this Communication were performed using a rotating-source/fixed-detector crossed molecular beams instrument located on the Chemical Dynamics Beamline at the Advanced Light Source. This instrument has been described in detail previously[1] and was configured for PTS measurements. Briefly, a pulsed molecular beam of ~5.8% vinyl chloride (Matheson, 99.5%) or ~1.8% propargyl chloride (Aldrich, 98%) seeded in helium was prepared using a pulsed valve with a heated nozzle. The molecular beam was skimmed once and intersected by a pulsed ArF excimer laser. The scattered photofragments accepted by the
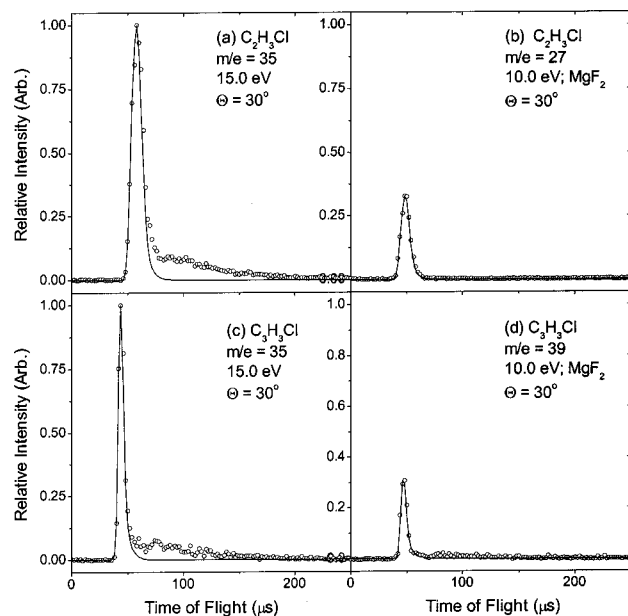
FIG. 1. TOF spectra at a source angle of 30° for (a) $m/e = 35$ (Cl$^+$) and (b) $m/e = 27$ (C$_2$H$_3^+$) from vinyl chloride, and TOF spectra for (a) $m/e = 35$ (Cl$^+$) and (b) $m/e = 39$ (C$_3$H$_3^+$) from propargyl chloride. Following normalization for experimental conditions, the polyatomic fragment TOF signal has been normalized with respect to the chlorine signal. In each case, open circles represent the data and the solid line represents the forward convolution fit to the data using the appropriate P(E$_T$) distribution shown in Fig. 2.
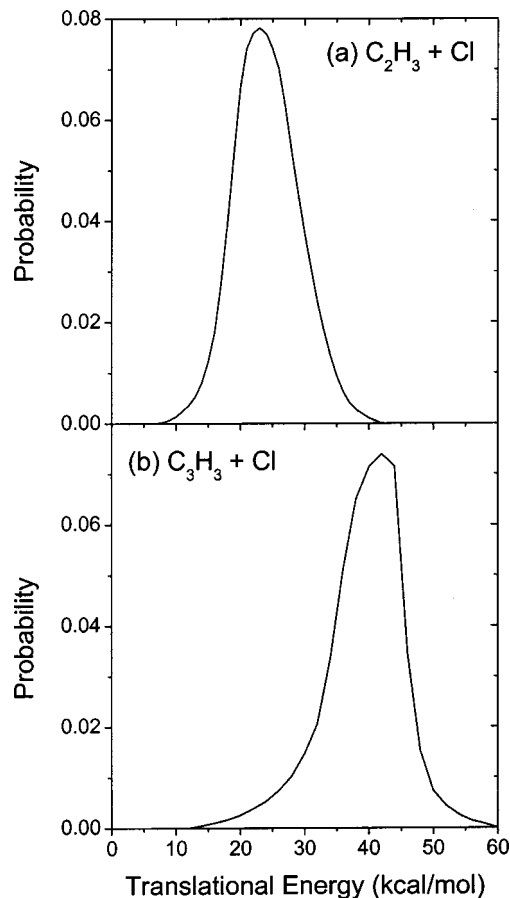

FIG. 2. Center of mass frame translational energy distributions for excited state atomic chlorine loss from (a) vinyl chloride and (b) propargyl chloride at 193 nm.

detector were ionized by tunable VUV synchrotron radiation, mass selected by a quadrupole mass filter, and counted as a function of time, producing angle-resolved time-of-flight (TOF) spectra for ions with a specific mass-to-charge ratio (m/e). The properties of the VUV radiation have been described elsewhere.[20] Two relevant features are that a rare gas filter was used to remove the higher harmonics of the undulator radiation,[20] and a MgF$_2$ window was placed in the path of the undulator radiation for photoionization energies below 10.8 eV to mitigate the effects of any residual high energy tail on the fundamental. The energy resolution ($\Delta E/E$) for the radiation was 2.3%.

Two types of photodissociation measurements were performed. First, a set of laboratory frame TOF spectra for two momentum-matched photofragments was acquired, which could be fit to yield a center of mass frame P(E$_T$) distribution. Second, a series of TOF spectra was obtained by fixing the laboratory angle, fixing the m/e to select the proper fragment signal, and stepping the undulator radiation. This series of measurements could be integrated (following normalization by VUV photon flux, laser shots, laser power, etc.) to produce a photoionization efficiency (PIE) curve, which shows the relative PI cross section as a function of photon energy. Both types of measurements have been reported in previous studies on this instrument, but here we illustrate the use of TOF measurements to yield absolute PI cross sections and place PIE curves on an absolute scale.

Figures 1(a) and 1(b) show representative TOF spectra for atomic chlorine ($m/e = 35$) and vinyl radical ($m/e = 27$) produced by photodissociation of vinyl chloride at 193 nm, while TOF spectra for atomic chlorine and propargyl radical

($m/e = 39$) from propargyl chloride photodissociation are presented in Figs. 1(c) and 1(d). For purposes of comparison, the TOF signal for the polyatomic fragment has been normalized to that of the atomic chlorine in each case. The TOF spectra from vinyl chloride dissociation are similar in appearance to those obtained by Blank et al.,[17] and the propargyl chloride spectra are similar to those obtained by Lee and Lin.[18] Additional TOF spectra were acquired at various laboratory angles for both fragments from each precursor, using photoionization energies of 10.0 and 15.0 eV for the hydrocarbon radical and Cl atom, respectively.

The TOF spectra presented in Fig. 1 were fit using the P(E$_T$) distributions shown in Fig. 2; the solid lines were obtained by forward convolution of the P(E$_T$) distribution with parameters characterizing the instrument.[21,22] Each P(E$_T$) distribution was obtained by point-wise adjustment until the TOF simulations simultaneously fit the entire series of TOF spectra. For vinyl chloride, the fit to the $m/e = 35$ TOF spectra shows the contribution that is momentum-matched to the $m/e = 27$ signal. The additional slow features in the $m/e = 35$ TOF spectra were shown by Blank et al.[17] to result from ground state dissociation to Cl + C$_2$H$_2$ + H and secondary decomposition of chlorovinyl radical; these features are not of interest to the current work because they are not momentum-matched to the vinyl signal. Similarly, TOF spectra for propargyl chloride were fit to include only the signal

resulting from the primary chlorine loss channel occurring on an excited electronic state.

By collecting spectra for each momentum-matched fragment at specific photoionization energies, scaling factors for normalizing the TOF spectra produced by forward convolution of the $P(E_T)$ distribution were obtained; these scaling factors are essentially the ratio of weighting factors necessary to reproduce observed lab frame TOF intensities by the $P(E_T)$ distribution. All kinematic effects are accounted for in the analysis. For the photodissociation process $C_2H_3Cl + h\nu_{193\,nm} \rightarrow C_2H_3 + Cl$, this procedure yields the relative cross section for momentum-matched fragments, i.e., $\sigma_{C_2H_3}(10\,eV)/\sigma_{Cl}(15\,eV)$, normalized for experimental conditions, including laser power, laser shots, VUV photon flux, and isotopic abundance (for chlorine, which was observed at $m/e = 35$ only). No correction for relative quadrupole transmission has been included, since the ion masses are similar and the correction has been found to be small.[4]

The photon energy of 15.0 eV for the Cl lies within the $Cl^+(^1D)$ continuum and is centered in a region where the photoionization cross section is relatively flat, as shown by Ruscic and Berkowitz.[13] In their work, the PIE of Cl was measured over an extended energy range and was put on an absolute scale using the average of a series of calculated cross sections just beyond the $Cl^+(^1S)$ edge at 16.4 eV. This average value, 40.2 Mb, yields $\sigma_{Cl} = 32.1$ Mb at 15.0 eV. Based on subsequent experimental and theoretical values, Berkowitz[8] recommends a slightly lower cross section of 34.2 Mb at the ^1S edge, which would yield $\sigma_{Cl} = 27.3$ Mb at 15.0 eV. This latter value lies close to a recent experimental measurement of 23 ± 2 Mb at 15.12 eV by Flesch et al.[16] based on Cl_2 photolysis. Using $\sigma_{Cl} = 27.3$ Mb, we find $\sigma_{C_2H_3} = 11.1$ Mb and $\sigma_{C_3H_3} = 8.3$ Mb at 10.0 eV, with estimated error bars of $\pm 20\%$. These values represent the average of measurements taken directly before and after data for PIE curves was recorded.

The PIE curve for vinyl radicals produced from the photodissociation of vinyl chloride at 193 nm is shown in Fig. 3(a). The points on the PIE curve were normalized by scaling to the absolute photoionization cross section of the vinyl radical at 10.0 eV, as related to atomic chlorine signal at 15.0 eV. Similarly, Fig. 3(b) presents the PIE curve for the propargyl radical from the 193 nm photodissociation of propargyl chloride; the points on the curve were scaled to the absolute photoionization cross section of the propargyl radical at 10.0 eV.

A key issue in this work is that the radicals do not undergo any collisions subsequent to photolysis of the precursor, and therefore have substantial internal excitation as determined by the photodissociation dynamics. For example, 193 nm excitation of vinyl chloride leaves ~55 kcal/mol to partition among translational and internal degrees of freedom of the photofragments.[17] The $P(E_T)$ distribution peaks at 23 kcal/mol, leaving 32 kcal/mol for internal excitation of the vinyl fragment. The most obvious manifestation of this excitation is the observation [Figs. 3(a) and 3(b)] of ion signal at photon energies below the radical ionization potentials, previously found to be 8.25 eV for vinyl[23] and 8.673 eV for propargyl.[24]
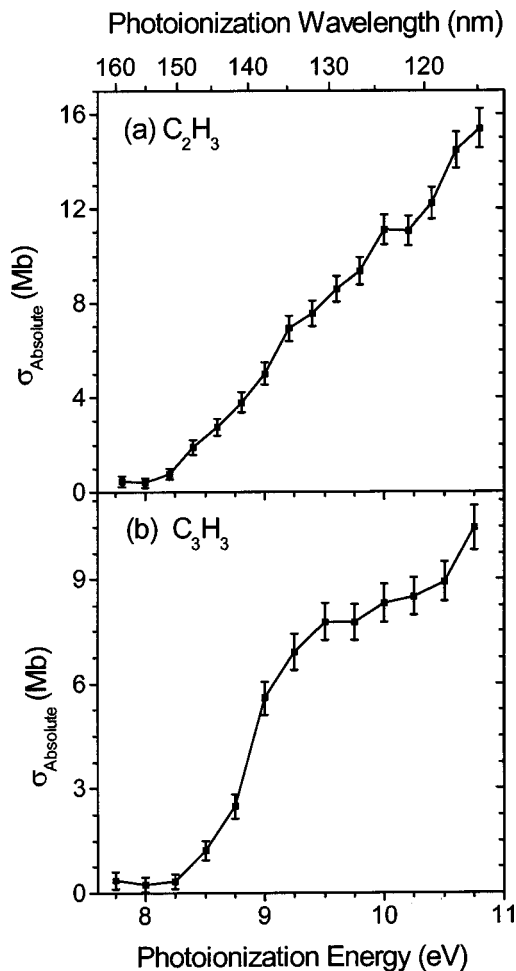

FIG. 3. Photoionization efficiency curves for (a) $m/e = 27$ ($C_2H_3^+$) from vinyl chloride and (b) $m/e = 39$ ($C_3H_3^+$) from propargyl chloride at a source angle of 30°. Solid squares represent the data points with 2σ error bars.

One must then consider the effect of internal excitation on the value of the photoionization cross section. For values above 9.2 eV, the shape of the PIE curve presented in Fig. 3(a) agrees extremely well with the (higher resolution) photoion yield spectrum presented by Berkowitz et al.[25] from pyrolysis of divinyl mercury at $T = ~1200$ K. On the other hand, when the two curves are superimposed, our PIE curve shows enhanced signal for values below 9.2 eV and has a photoionization onset at a lower energy, owing to the difference in internal energy of the vinyl products in each experiment. For C_2H_3 produced in the current experiment, $nkT = ~32$ kcal/mol of internal energy distributed into $n = 9$ vibrational degrees of freedom corresponds to $T = ~1800$ K. This comparison indicates that near the IP our cross section values are too high, because the additional vibrational excitation of the polyatomic fragment can redshift the PIE curve. However, by 10 eV, the effect of internal excitation on the cross section is quite small.

As mentioned earlier, reference spectra were recorded before and after PIE measurements were obtained and averaged in order to reduce potential systematic error in the measurements, such as from slight pressure fluctuations in the rare gas cell. Also, the data were not corrected for the mass-dependent quadrupole transmission function, which should

be on the order of 10%. The data were not corrected for the VUV calorimeter response function, which was taken to be linear. Additionally, cracking of the polyatomic fragments should be minimal, since the threshold for dissociative ionization of vinyl and propargyl radicals should occur at ~13 eV for the lowest energy route in each case.[26,27] Finally, error could arise from error in the Cl reference cross section. The recent measurements by Flesch et $al.$[16] of the absolute PI cross section for Cl at 14.60 and 15.12 eV agree to within 15–20% of the cross section at 15 eV extrapolated from the value recommended by Berkowitz[8] for the ^1S edge. In light of these factors and the presence of vibrational excitation of the polyatomic fragments, the reported values at 10 eV should be reliable to within 20% of the true value.

The most striking finding from these experiments is the clear difference in absolute photoionization cross sections for vinyl radical versus propargyl radical as the photoionization energy is increased above threshold. Comparing Figs. 3(a) and 3(b) at 10.0 eV, the absolute photoionization cross section for vinyl radical is approximately one third larger than that for propargyl radical. Clearly, knowledge of absolute photoionization cross sections is important for comparison of signal levels of radicals produced by photoionization.

In the future, this technique will be extended to study additional radical species, which are important in combustion and flame processes, with the goal of constructing a database of absolute photoionization cross sections. Such a database can allow researchers to quantify the production of radical species more accurately, leading to an improved understanding of physical processes.

[1] X. Yang, D. A. Blank, J. Lin, A. M. Wodtke, A. G. Suits, and Y. T. Lee, Rev. Sci. Instrum. **68**, 3317 (1997).
[2] J. A. Mueller, B. F. Parsons, L. J. Butler, F. Qi, O. Sorkhabi, and A. G. Suits, J. Chem. Phys. **114**, 4505 (2001).
[3] J. C. Robinson, W. Sun, S. A. Harris, F. Qi, and D. M. Neumark, J. Chem. Phys. **115**, 8359 (2001).
[4] J. C. Robinson, S. A. Harris, W. Sun, N. E. Sveum, and D. M. Neumark, J. Am. Chem. Soc. **124**, 10211 (2002).
[5] W. S. McGivern, O. Sorkhabi, A. G. Suits, A. Derecskei-Kovacs, and S. W. North, J. Phys. Chem. **104**, 10085 (2000).
[6] T. A. Cool, T. A. Mostefaoui, F. Qi, A. McIlroy, P. R. Westmoreland, M. E. Law, L. Poisson, D. S. Peterka, and M. Ahmed, J. Chem. Phys. (to be published).
[7] J. W. Gallagher, C. E. Brion, J. A. R. Samson, and P. W. Langhoff, J. Phys. Chem. Ref. Data **17**, 9 (1988).
[8] J. Berkowitz, *Atomic and Molecular Photoabsorption: Absolute Total Cross Sections* (Academic, San Diego, CA, 2002).
[9] E. R. Brown, S. L. Carter, and H. P. Kelly, Phys. Rev. A **21**, 1237 (1980).
[10] S. S. Tayal, Phys. Rev. A **47**, 182 (1993).
[11] M. Y. Amusia, N. A. Cherepkov, L. V. Chernysheva, and S. T. Manson, Phys. Rev. A **61**, 020701 (2000).
[12] P. M. Dehmer, J. Berkowitz, and W. A. Chupka, J. Chem. Phys. **59**, 5777 (1973).
[13] B. Ruscic and J. Berkowitz, Phys. Rev. Lett. **50**, 675 (1983).
[14] J. A. R. Samson, Y. Shefer, and G. C. Angel, Phys. Rev. Lett. **56**, 2020 (1986).
[15] W. J. van der Meer, R. J. Butselaar, and C. A. de Lange, Aust. J. Phys. **39**, 779 (1986).
[16] R. Flesch, J. Plenge, S. Kuhl, M. Klusmann, and E. Ruhl, J. Chem. Phys. **117**, 9663 (2002).
[17] D. A. Blank, W. Z. Sun, A. G. Suits, Y. T. Lee, S. W. North, and G. E. Hall, J. Chem. Phys. **108**, 5414 (1998).
[18] Y. R. Lee and S. M. Lin, J. Chem. Phys. **108**, 134 (1998).
[19] R. Flesch, M. C. Schurmann, J. Plenge, M. Hunnekuhl, H. Meiss, M. Bischof, and E. Ruhl, Phys. Chem. Chem. Phys. **1**, 5423 (1999).
[20] A. G. Suits, P. Heimann, X. M. Yang, M. Evans, C. W. Hsu, K. T. Lu, Y. T. Lee, and A. H. Kung, Rev. Sci. Instrum. **66**, 4841 (1995).
[21] X. Zhao, Ph.D. thesis, University of California, Berkeley, 1988.
[22] J. D. Myers, Ph.D. thesis, University of California, Berkeley, 1993.
[23] J. A. Blush and P. Chen, J. Phys. Chem. **96**, 4138 (1992).
[24] T. Gilbert, R. Pfab, I. Fischer, and P. Chen, J. Chem. Phys. **112**, 2575 (2000).
[25] J. Berkowitz, C. A. Mayhew, and B. Ruscic, J. Chem. Phys. **88**, 7396 (1988).
[26] NIST Chemistry WebBook NIST Standard Reference Database Number 69, Eds. P. J. Linstrom and W. G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg, MD, 20899 (http://webbook.nist.gov).
[27] J. A. Miller and C. F. Melius, Combust. Flame **91**, 21 (1992).