J. Braz. Chem. Soc., Vol. 7, No. 2, 91-95, 1996.
Printed in Brazil.

0103 – 5053 $6.00 + 0.00

Photoabsorption Cross Sections Derived by the Electron Energy Loss Spectroscopy Technique for Ammonia, Methane and Acetylene in the Photon Energy Range of 5 to 100 eV

A.C.A. Souza[a] *and S.K. Srivastava*[b]*

[a]*Instituto de Química, UFRJ, Cidade Universitária, 21949-900 Rio de Janeiro - Brazil*
[b]*Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, California, 91109, USA*

Received: December 22, 1994; August 8, 1995

Seções de choque de fotoabsorção para NH_3, CH_4 e C_2H_2 foram obtidas na região entre 5 e 100 eV (250 e 12.5 nm) utilizando-se a técnica de perda de energia de elétrons. Os resultados são comparados a dados obtidos na literatura. A concordância dos resultados é boa, em geral. O presente trabalho fornece medidas de fotoabsorção naqueles comprimentos de onda em que não há registros de medidas anteriores.

Photoabsorption cross sections for NH_3 , CH_4 and C_2H_2 were obtained in the photon energy range of 5 to 100 eV (250 and 12.5 nm) by utilizing the electron energy loss spectroscopy (EELS) technique. They are compared with previously reported data. In general, the agreement is good. The present work provides photoabsorption data at wavelengths where no previous measurements have been made.

Keywords: *photoabsorption, ammonia, methane, acetylene*

Introduction

Photoabsorption cross sections for NH_3, CH_4 and C_2H_2 are important for modeling planetary and cometary atmospheres, for plasmas utilized for deposition of diamond films, and for understanding combustion chemistry. Although these cross sections have been measured since the 1930s by utilizing various light sources, it is only during the last two decades that extensive use has been made of synchrotron radiation for this purpose. The advantage of synchrotron radiation lies in the fact that photoabsorption cross sections can be obtained over a large continuous wavelength range with a high resolution. Lassettre and co-workers[1] pioneered a technique which utilizes the well-known technique of electron energy loss spectroscopy, EELS, based on zero moment transfer. This technique also generates photoabsorption cross sections similar to those obtained by synchrotron radiation. However, in order to generate accurate values have to be normalized of absolute cross sections relative values at least at one wavelength by a cross section obtained by a photoabsorption experiment performed by utilizing a light source. In some cases the energy loss spectroscopy technique is advantageous because it fills the gaps in the photoabsorption data obtained by light sources which emit discrete wavelengths or by the synchrotron source. It is also useful for obtaining cross section values of those materials which are difficult to prepare in the form of vapors for the light absorption technique. Therefore, the Energy Loss Technique is sometimes called the "poor man's synchrotron technique".

In this paper we present photoabsorption data utilizing the EELS technique and compare them with the previously available data. As will be clear from the results and discussion, we have not only extended the wavelength range beyond the previous measurements, but have also filled the gaps in the data. It must be pointed out here that the data presented here is specifically meant for modeling purposes, and no effort has been made to perform high resolution spectroscopic studies.

Apparatus and Method

Details on the apparatus used and the method of data reduction and conversion of EELS into photoabsorption cross sections can be found in our recent publication[2].

Briefly, the apparatus consists of an electron gun which produces an energy selected electron beam of energy varying from 500 to 1000 eV. The gas jet is formed by a hypodermic needle and crosses the electron beam at a right angle. Scattered electrons are then energy analyzed by the use of a Molenstedt velocity analyzer[3], which is fitted with a channeltron electron multiplier and conventional pulse counting electronics for recording the EELS. The electron gun can be rotated around the molecular beam, which allows the EELS to be obtained for different scattering angles. It can be changed in the range of -60 to +60° with a 1/60° step. All of these components are housed in a scattering chamber which is pumped by a 6 diffusion pump. All metal surfaces inside the chamber are coated with colloidal graphite in order to minimize contributions from secondary electrons. The magnetic field in the scattering region is reduced to about 5 mG by utilizing three pairs of orthogonal square Helmholtz coils.

The EELS is obtained by selecting the energy of our electron gun at 1 KeV with full width at half maximum (FWHM) of 0.5 eV and a current of 50 nA. Before recording the data, the whole system is aligned by a He-Ne laser. The zero degree angle is experimentally determined by recording the intensity of the elastically scattered electrons on both positive and negative sides of the nominal zero degree scattering angle. The energy loss scale is calibrated by the use of the well-known transition 1s - 2p of He at 21.22 eV. The maximum energy loss which was recorded was 100 eV.

The method of obtaining photoabsorption cross sections by using this apparatus is as follows. First, an energy loss spectrum is recorded. This spectrum represents relative values of intensities, $I_n(E)$, of electrons scattered at 0° with respect to the direction of the incident electron beam. If $I_n(E)$ corresponds to the continuum part of the spectrum, then the following definition can be made,

$$\frac{dI_n}{dE} = C_1 \frac{d}{dE}\left[\frac{d\sigma_n(E)}{d\Omega}\right] \quad (1)$$

where C_1 is a constant derived by Srivastava *et al.*[4] (1975), E is the excitation energy (or energy lost by the incident electron) represented here as a continuous variable, $d\sigma_n(E)/dE$ is the density of the cross section (Inokuti, 1971)[5], and Ω is the solid angle subtended by the scattered electron detector at the scattering center. This density is related to the apparent generalized oscillator strength distribution (Kuyatt, 1968)[6] by:

$$\frac{df^g}{dE} = \left[\frac{1}{2a_0^2}\right]\left[\frac{E_n}{E_{at}}\right]\left[\frac{P_1}{P_2}\right](\Delta P)^2\left[\frac{d}{dE}\frac{dI_n(E)}{d\Omega}\right] \quad (2)$$

where a_0 is the Bohr radius (5.292×10^{-9} cm), E_n is the energy loss in eV, $E_{at} = 27.21$ eV, P_1 and P_2 are the initial and final momenta of the scattered electron, respectively, and ΔP is the vector change in the momentum of the colliding electron.

Lassettre *et al.* (1969)[1] showed that f^G approaches the optical oscillator strength at the limit when $\Delta P \rightarrow 0$ regardless of whether the Born approximation holds. This implies that low energy electron beams and EELS obtained at small scattering angles can be employed for generating an energy loss spectrum and for converting it into a photoabsorption spectrum. Therefore, for sufficiently small values of ΔP, the following relations can be written:

$$\frac{df^G}{dE} \equiv \frac{df^{opt}}{dE}$$

where

$$\frac{df^{opt}}{dE} \equiv \frac{1}{\beta} \times \sigma(E) \quad (3)$$

Here, β is a proportionality constant, the value of which is 1.098×10^{-16} cm^2 eV, and $\sigma(E)$ is the photoabsorption cross section for a photon energy of E(ev). Thus, from the energy loss spectrum recorded for a sufficiently small value of ΔP, the photoabsorption cross sections can, in principle, be obtained. However, the Möllenstedt analyzer subtends a finite solid angle in the collision region. Therefore, the intensity of scattered electrons, normally detected at about a 2° scattering angle, is integrated over this solid angle. This necessitates the correction for I_n in Eq. 2. Further details on this can be found in our previous publication[2].

Ideally, by utilizing Eqs. 2 and 3 it should be possible to obtain absolute values of photoabsorption cross sections. However, in practice there are many unknown parameters, such as the transmission efficiency of the EELS analyzer of the detector solid angle, which cannot be accurately determined. Therefore, the relative shape of the photoabsorption curve obtained by converting the EELS through Eqs. 2 and 3 is normalized with a previously measured cross section value at least at one wavelength. This procedure then gives the absolute values of cross sections at other wavelengths. We have followed this method of normalization for NH_3, C_2H_2 and CH_4. The wavelengths at which the relative shapes of the photoabsorption curves have been normalized will be given in the next section.

Results and Discussion

The EELS spectra for NH_3, C_2H_2 and CH_4 were obtained at a 1 KeV electron impact energy and a 2° scattering angle. They were then converted into photoabsorption spectra by the method described in the previous section. They are presented in Figs. 1, 2 and 3, respectively. In the following we will discuss each molecule separately and compare our data with previous measurements.

Table 1. Normalized values of photoabsorption cross sections for ammonia as a function of photon energy in the range of 11 to 100 eV.

Photon energy (eV)	σ (x 10^{-18} cm^2)	Photon energy (eV)	σ (x 10^{-18} cm^2)
11	10.0	37	11.5
12	21.0	38	10.5
13	18.0	39	10.0
14	16.0	40	9.5
15	27.0	41	9.0
16	31.0	42	8.5
17	32.0	43	8.0
18	31.5	44	7.5
19	31.0	45	7.0
20	30.0	46	6.5
21	27.5	47	6.3
22	26.0	48	6.0
23	24.5	49	5.5
24	23.5	50	5.0
25	22.5	55	4.0
26	21.5	60	3.5
27	20.0	65	3.0
28	19.0	70	2.5
29	18.5	75	2.2
30	17.0	80	2.0
31	16.5	85	1.8
32	16.0	90	1.5
33	15.0	95	1.3
		100	1.2

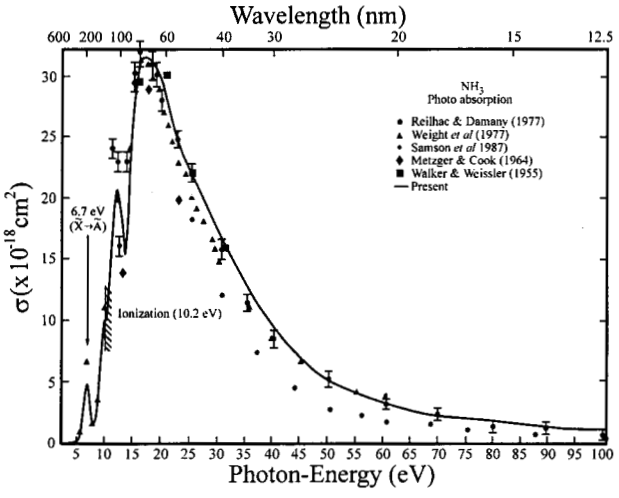

Figure 1. Photoabsorption cross sections of ammonia derived by EELS technique.

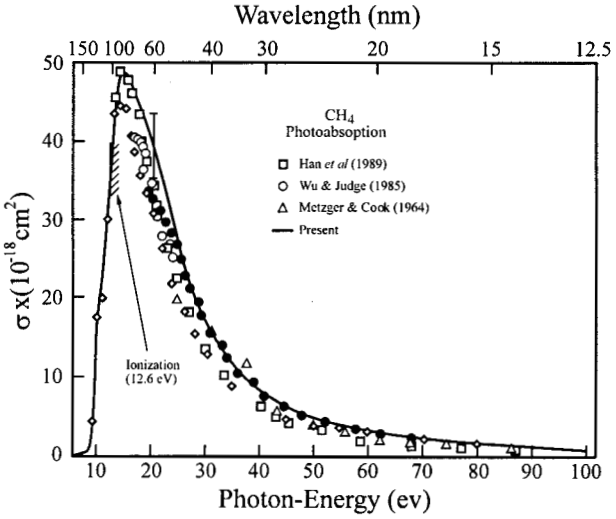

Figure 2. Photoabsorption cross sections of methane derived by EELS technique.

Table 2. Normalized values of photoabsorption cross sections for methane as a function of photon energy in the range of 10 to 100 eV.

Photon energy (eV)	σ (x 10^{-18} cm^2)
10	10.0
12	28.1
14	47.1
16	48.3
18	44.5
20	40.0
22	35.9
24	30.0
26	25.1
28	22.0
30	17.5
35	12.4
40	8.3
45	6.3
50	5.1
55	3.8
60	3.3
65	2.8
70	2.3
75	2.0
80	1.8
85	1.5
90	1.3
95	1.0
100	0.7

NH_3:

We utilized the Samson *et al.*[7] value for a photon energy of 23 eV for the purpose of normalization. Their data at other wavelengths, along with the results of Weight *et al.*[8], Reilhac and Damany[9], Metzeger and Cook[10], and Walker and Weissler[11] are shown in Fig. 1. Table 1 presents our cross section numerical values as a function of photon energy.

As is clear from Fig. 1, the results of Samson *et al.*[7] agree very well with Weight *et al.*[8], except in a narrow photon energy range lying between energies of 10.2 eV (1212.69 A) and 12 eV (1033.33 A). Our normalized values compare very well with the results of Samson *et al.* (within the experimental errors of the two measurements) between the photon energies of 15 eV and 100 eV. The error bars on the Samson *et al.* results are shown in Fig. 1. Present data are accurate to within 5%. For photon energies less than 12 eV our values agree well with the values of Weight *et al.*[8]

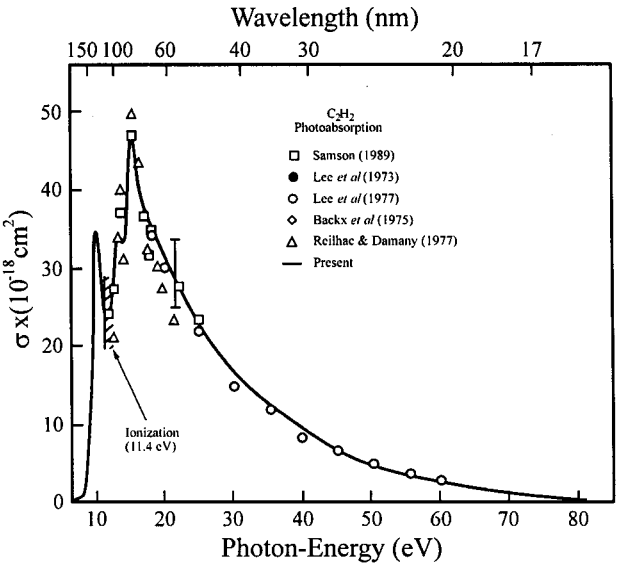

Figure 3. Photoabsorption cross sections of acetylene derived by EELS technique.

Table 3. Normalized values of photoabsorption cross sections for acetylene as a function of photon energy in the range of 10 to 80 eV.

Photon energy (eV)	σ (x 10^{-18} cm^2)
10	34.8
12	24.8
14	33.5
16	46.3
18	37.6
20	31.6
22	28.2
24	25.9
26	22.7
28	20.0
30	16.7
35	12.8
40	9.4
45	6.5
50	4.7
55	3.7
60	2.6
65	1.8
70	1.3
75	0.8
80	0.5

CH_4:

Figure 2 shows the present data along with the results from previous measurements. They were normalized to the

most recent photoabsorption value of Samson *et al.* (1989)[12] at 14.4 eV. There are several measurements on CH_4 photoabsorption cross sections reported prior to 1975. They have not been included in Fig. 2 since they have been compared in the references cited. Various data agree well with each other within the error bars of each experiment. Tabulated data are presented in Table 2.

C_2H_2:

Figure 3 shows the present results along with previous measurements. Our data are normalized at 25 eV with the photoabsorption cross section of Han *et al.* (1989)[13]. Again, within the experimental error all previous measurements presented here are in good agreement with each other. Table 3 presents the tabulated data.

Conclusions

We were able to generate normalized values of photoabsorption cross sections for three important molecules by utilizing the high energy electron loss spectroscopy (EELS) technique. We were also able to present cross section data in wavelength regions where no previous data existed. Although the wavelength resolution obtained by this technique is not as good as that achieved by optical absorption spectroscopy the data are quite useful for modeling planetary atmospheres and low temperature plasmas employed for semiconductor processing.

Acknowledgments

We gratefully acknowledge CNPq (Brazil) and NSF (USA) for funding this research project.

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