

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/245119694>

Photodissociation thresholds of OH produced from CH₃OH in solid neon and argon

ARTICLE *in* NUCLEAR INSTRUMENTS AND METHODS IN PHYSICS RESEARCH SECTION A ACCELERATORS SPECTROMETERS DETECTORS AND ASSOCIATED EQUIPMENT · JULY 2001

Impact Factor: 1.22 · DOI: 10.1016/S0168-9002(01)00685-4

CITATIONS

5

READS

8

4 AUTHORS, INCLUDING:



Bing-Ming Cheng

National Synchrotron Radiation Research Ce...

158 PUBLICATIONS **2,140** CITATIONS

SEE PROFILE



ELSEVIER

Nuclear Instruments and Methods in Physics Research A 467–468 (2001) 1461–1464

NUCLEAR
INSTRUMENTS
& METHODS
IN PHYSICS
RESEARCH
Section A

www.elsevier.com/locate/nima

Photodissociation thresholds of OH produced from CH₃OH in solid neon and argon

Bing-Ming Cheng^{a,*}, Chin-Ping Liu^a, Wen-Jui Lo^b, Yuan-Pern Lee^c

^a *Synchrotron Radiation Research Ctr, Research Group, No. 1 R&D Road VI, Hsinchu Science-Based Industrial Park, Hsinchu 300, Taiwan*

^b *Department of Nursing, Tzu Chi College of Technology, 880, Sec. 2, Chien Kuo Road, Hualien 970, Taiwan*

^c *Department of Chemistry, National Tsing Hua University, 101, Sec. 2, Kuang Fu Road, Hsinchu 300, Taiwan*

Abstract

Photodissociation thresholds of OH from CH₃OH in solid Ne and Ar were determined via photolysis of CH₃OH/Ne and CH₃OH/Ar (1/200) samples in situ at 4 K. The samples were irradiated with VUV synchrotron radiation after dispersion by a Seya-Namioka monochromator. The OH photo-product was detected by means of laser-induced fluorescence technique. The increase of fluorescent intensity of OH was monitored and recorded after the matrix sample was irradiated at different wavelengths for 3–5 min. Photodissociation threshold energies of 7.13 ± 0.02 eV (174.0 ± 0.5 nm) and 7.08 ± 0.04 eV (175.0 ± 1.0 nm) were measured for OH production of CH₃OH in solid Ne and Ar, respectively. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 33.80.Gj; 35.20.Gs; 42.62.Fi; 82.50.Fv

Keywords: Methanol; Hydroxyl; Photodissociation threshold; Matrix isolation

1. Introduction

Matrix-isolation techniques have yielded valuable information about free radicals and other transient species [1–3]. The techniques are applied extensively to acquire spectra of these species and complement data of the gaseous phase [4–9]. Of various methods to generate free radicals in solid matrices, photodissociation of suitable precursors deposited in a matrix by means of UV/VUV radiation is the most direct approach. However, the photochemistry of molecules isolated in

matrices differs from that in the gaseous phase, because a solid matrix environment modifies the photophysical behavior of the guest molecules in many ways. As consequence the dynamics of reactions following photodissociation in a matrix remain incompletely understood and photodissociation of molecules isolated in matrices has become the focus of both experiments and theory.

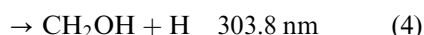
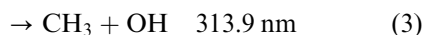
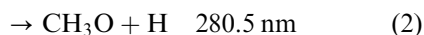
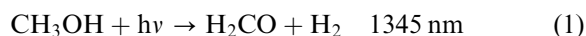
The rigid environment impeding molecular photodissociation is an important perturbation in a solid matrix. An increased threshold energy of photodissociation of matrix-isolated molecules is typically observed. For example, in experiments on photodissociation of H₂O in solid Ne, Ar, Kr or Xe, threshold energies for production of OH were determined to be 1.3–1.8 eV greater than that in

*Corresponding author. Tel.: +886-3-578-028; fax: +886-3-578-9816.

E-mail address: bmcheng@src.gov.tw (B.-M. Cheng).

the gaseous phase, 5.118 eV, determined by workers at BESSY and our group [10–13]. In further work on the dynamics of photolysis in a matrix, we investigated CH₃OH as a target molecule.

Photolysis of CH₃OH in matrices is not well established. The threshold wavelengths for possible channels of photolysis in the gaseous phase are:



Assessing the photolysis thresholds for each channel is important for an understanding of matrix effects such as perturbation of absorption and the cage effect. Comparison of the photodissociation threshold of these channels between gaseous and matrix-isolated CH₃OH is expected to increase insight into these matrix effects.

2. Experiment

We determined the threshold for photodissociation by dissociating a matrix sample in situ on scanning the energy of synchrotron radiation and by detecting the increase in intensity of fluorescence of the generated product of photolysis. Synchrotron radiation from the 1.5 GeV storage ring at Synchrotron Radiation Research Center in Taiwan was dispersed with a 1-m Seya-Namioka monochromator. The experimental arrangement is described in detail in previous reports [13–15]. To suppress light of higher order from the diffraction grating, we used a LiF filter window (thickness 2 mm) to separate the cryostat system from the monochromator. During exposure of the solid sample, the slitwidth of the beam line was typically set at 0.2 mm corresponding to a nominal resolution 0.5 nm.

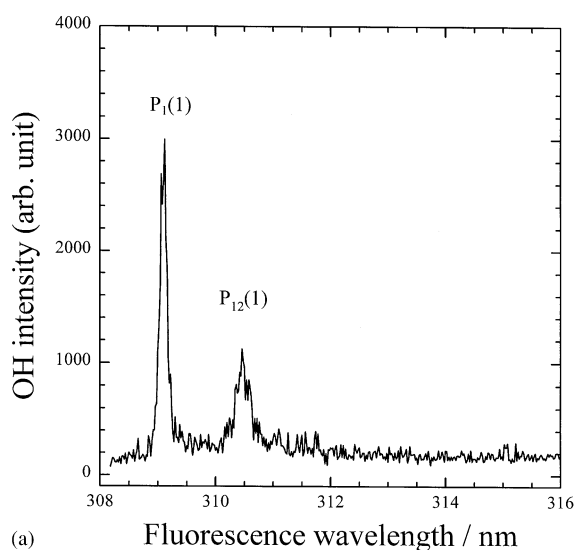
A mixed gaseous sample of CH₃OH/Ne (Ar) was condensed onto a LiF window maintained at 4 K. The synchrotron light intersected the LiF window at an angle of about 45°. A laser beam was incident in the direction opposite to that of the synchrotron radiation, and emission was dispersed

with a monochromator in a direction perpendicular to that of the beam from the laser (Nd:YAG/dye laser system). To determine the threshold of photodissociation, we adjusted the laser at a particular wavelength for excitation and set the dispersing monochromator at a particular emission feature of the photo-product. Then the fluorescent intensity of the photo-product was monitored by scanning the radiation for photodissociation from the synchrotron in the direction of decreasing wavelength (increasing energy) in steps 0.5 nm. After exposing the solid sample to VUV radiation for 3–5 min at each step the fluorescent intensity of the photo-product was recorded.

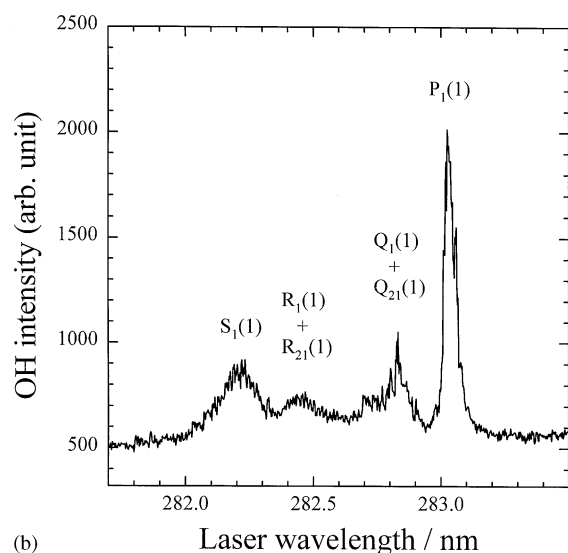
3. Results

To establish the probing conditions for possible photo-products, we investigated CH₃O, CH₂O and OH in matrices by means of their fluorescence. For example, Fig. 1a shows a dispersed fluorescence spectrum of an irradiated sample, CH₃OH/Ne = 1/200, with excitation at 283 nm; Fig. 1b shows an excitation spectrum of the same matrix observed on monitoring emission near 309 nm. The dispersed fluorescence and the fluorescence excitation spectra of OH isolated in solid Ar were also recorded; the positions of spectral lines vary slightly with matrix.

To determine the threshold of OH for photodissociation of CH₃OH in solid Ne, we set the laser to the P₁(1) line of a transition A(v' = 1) ← X(v'' = 0) of OH at 283.045 nm and the monochromator at 309.0 ± 5.0 nm to observe fluorescence of OH. The fluorescent intensity of OH was monitored as the energy of the synchrotron radiation was scanned in the direction of increasing energy in steps of 0.5 nm from 185 to 160 nm. After exposing the sample to VUV radiation for 5 min at each step the fluorescent intensity of OH was recorded. The result is shown in Fig. 2. According to Fig. 2, the photodissociation threshold of OH from CH₃OH in solid Ne is determined to be 174.0 ± 0.5 nm, corresponding to dissociation energy 7.13 ± 0.02 eV. The threshold is determined by the intersection of the baseline with the rising signals fitted to a non-linear exponential curve; the



(a)



(b)

Fig. 1. (a) Fluorescence spectrum of OH in solid Ne when excited at 283.045 nm. (b) Excitation spectrum of OH in solid Ne monitored at 309 nm.

error includes the uncertainties from a nominal resolution and statistical deviation in experimental data. The threshold of OH from CH_3OH in solid Ar was investigated on setting the excitation laser at 285.0 nm and observing OH emission near 340 nm. The result is shown in Fig. 3. The threshold in solid Ar was obtained to be 175 ± 1 nm, corresponding to dissociation energy 7.08 ± 0.04 eV. Hence thresholds for photoproduction of OH

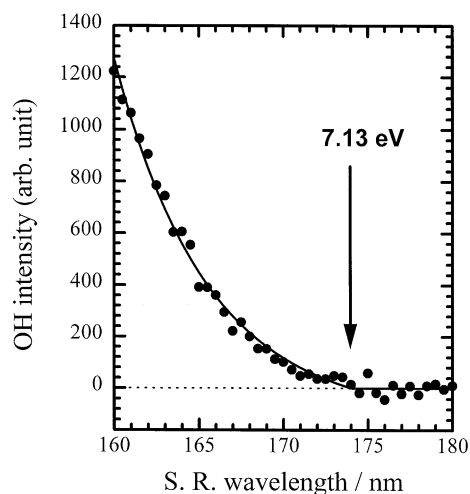


Fig. 2. Increase of fluorescent intensity of OH in solid Ne versus photodissociation wavelength scanned in decreasing direction for equal periods of irradiation. Fluorescence of OH was probed at 309 nm when excited at 283.045 nm. The solid line is a fitting curve. The arrow indicates the energy at the dissociation threshold.

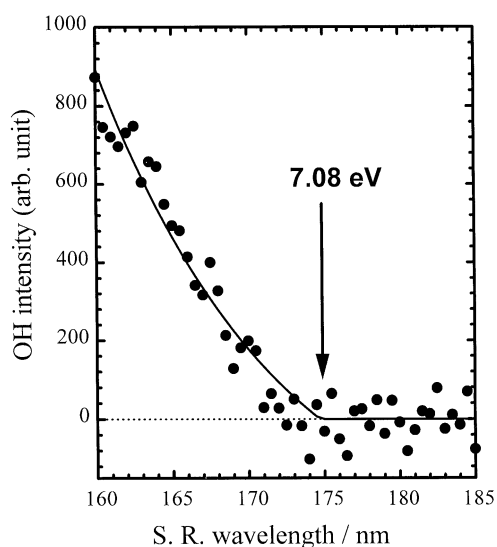


Fig. 3. Increase of fluorescent intensity of OH in solid Ar versus photodissociation wavelength scanned in decreasing direction for equal periods of irradiation. Fluorescence of OH was probed at 340 nm when excited at 285.0 nm. The solid line is a fitting curve. The arrow indicates the energy at the dissociation threshold.

from CH₃OH in Ne and Ar matrices are 3.18 and 3.13 eV, respectively, greater than that in the gaseous phase, 3.950 eV, because of matrix effects.

We tried to detect CH₃O and CH₂O after photolysis of CH₃OH, but signals with too poor signal to noise ratio precluded determination of the threshold. The small yields of these two channels are consistent with previous observations after photolysis of CH₃OH at 85 K [16].

Acknowledgements

We thank the Synchrotron Radiation Research Center in Taiwan and the National Science Council of the Republic of China for support.

References

- [1] M.J. Almond, A. Downs, *Spectroscopy of Matrix Isolated Species*, Wiley, New York, 1989.
- [2] L. Andrews, M. Moskovits (Eds.), *Chemistry and Physics of Matrix-Isolated Species*, North-Holland, Amsterdam, 1989.
- [3] A.J. Barnes, W.J. Orville-Thomas, A. Muller, R. Gaufres, (Eds.), *Matrix Isolation Spectroscopy*, Reidel, London, 1980.
- [4] L. Andrews, in: A.J. Barnes, W.J. Orville-Thomas, A. Muller, R. Gaufres, (Eds.), *Matrix Isolation Spectroscopy*, Reidel, London, 1980, Chapter 2.
- [5] V.E. Bondybey, T.A. Miller, in: *Spectroscopy of Matrix Isolated Species*, Wiley, New York, 1989, Chapter 6.
- [6] M.E. Jacox, W.E. Thompson, *J. Chem. Phys.* 91 (1989) 1410.
- [7] D. Forney, M. Jakobi, J.P. Maier, *J. Chem. Phys.* 90 (1989) 600.
- [8] D.M. Hudgins, S.A. Sandford, L.J. Allamandola, *J. Phys. Chem.* 98 (1994) 4243.
- [9] T.M. Halasinski, J.T. Godbout, J. Allison, G.E. Leroi, *J. Phys. Chem.* 98 (1994) 3930.
- [10] R. Schrieffer, M. Chergui, H. Kunz, V. Stepanenko, N. Schwentner, *J. Chem. Phys.* 91 (1989) 4128.
- [11] R. Schrieffer, M. Chergui, O. Unal, N. Schwentner, V. Stepanenko, *J. Chem. Phys.* 93 (1990) 3245.
- [12] R. Schrieffer, M. Chergui, N. Schwentner, *J. Phys. Chem.* 95 (1991) 6124.
- [13] B.-M. Cheng, W.-J. Lo, L.-H. Lai, W.-C. Hung, Y.-P. Lee, *J. Chem. Phys.* 103 (1995) 6303.
- [14] B.-M. Cheng, W.-J. Lo, W.-C. Hung, *Chem. Phys. Lett.* 236 (1995) 355.
- [15] B.-M. Cheng, *J. Phys. Chem.* 100 (1996) 8200.
- [16] J.G. Calvent, J.N. Pitts, Jr., *Photochemistry* 1996.