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TITLE

LIFETIME AND QUENCHING MEASUREMENTS OF C_2H EMISSION PRODUCED BY VACUUM ULTRAVIOLET PHOTOLYSIS OF C_2H_2

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LIFETIME AND QUENCHING MEASUREMENTS OF C_2H EMISSION PRODUCED BY VACUUM ULTRAVIOLET PHOTOLYSIS OF C_2H_2

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Abstract

The state-of-the-art tunable vuv sources are used to produce excited C_2H photofragments (C_2H^*) via the photolysis of acetylene molecules. The quenching rate constants of the C_2H emission by a number of species are determined. The collision-free fluorescence lifetimes are measured at different excitation wavelengths. The excitation energy threshold for producing the observed emission is determined. In addition, a correlation between the excitation energy and the emission wavelength is observed.

Introduction

In the past, the lack of spectrally intense and tunable vuv sources has made it extremely difficult to investigate spectroscopy and photochemical dynamics of gas-phase species in the short wavelength region ($\lesssim$200 nm). Large vacuum monochromators (several meters in length) are used to maximize the throughput of the photon flux and spectral resolution. Generally, there is a tradeoff between photon flux and resolution. A monochromatic vuv source typically is very weak and in most cases only absorption techniques can be employed to examine spectroscopic features of a species. More recently, the technological advances provided by synchrotron light sources and vuv laser generation in non-linear media have led to many new prospects in the investigation of photophysics and photochemistry of high-lying states of molecules. In this paper, we will discuss the application of these novel vuv sources in the photolysis of the acetylene molecule to produce the elusive C_2H radicals.

The C_2H radical is thought to be an important intermediate in combustion processes including sooting flames[1] as well as interstellar clouds[2] and planetary atmospheres.[3] Because it is a simple radical isoelectronic with the well known CN radical it might be expected to have simple spectroscopic features. Calculations show, however,[4] that the bending and stretching vibrational modes mix several low-lying electronic states. The complexity of the spectrum is confirmed by the near infrared observations.[5]

Acetylene photolysis is thought to be a good source of C_2H radicals.[6,7] Diacetylene, C_4H_2, is the major product of C_2H_2 photolysis in the vacuum ultraviolet[8] and C_2H is the intermediate in this process. Becker et al.[9] first observed photoproduct emission following acetylene photolysis at 1236 Å. This photoproduct emission appeared to be a continuum from 400 nm to 580 nm. There seems to be little doubt that the continuum emission is due to C_2H^*.[10] Similar emission has been seen from the photolysis of C_2H_2, C_2HBr, and C_2HCF_3.[11] Production of ground state C_2H is also observed in matrix experiments.[12] The work by Becker et al. has deduced an emission lifetime of 6 μs using a fluorescence phase modulation technique. A controversy has arisen over the mechanism of this long decay time: does it represent the radiative lifetime of C_2H^* or of a dark intermediate state that produces a rapidly emitting C_2H^* product.[7,10]

A proposal[13,14] for the dark intermediate state is that it is the lowest triplet state of vinylidene, CCH_2.[15-17] Vinylidene has been observed by flash photolysis of acetylene followed by absorption at 140 and 157 nm.[13] The lowest triplet state of the acetylene isomer, vinylidene is calculated to be at 14,700 cm^{-1} above the ground state.[15] If a triplet state is the dark precursor to the C_2H^* emission, it might be expected this intermediate would be quenched more efficiently by species containing heavy atoms that have a large spin orbit splitting. It is the intention of this paper to address the issues of the collision-free fluorescence lifetime and the quenching efficiency of the emission produced by vuv photolysis of the acetylene molecule.

Experimental

Two kinds of experimental apparatus are used for these experiments. A synchrotron light source is used for obtaining low-resolution excitation spectra over the tuning range from 110 nm to 40 nm. For the time-resolved measurements of fluorescence decay and high-resolution excitation spectra covering a single vibronic state, a tunable dye laser is frequency tripled in inert gases (Xe, Kr, and Ar) to produce tunable vuv pulses.[18-22]

The synchrotron light source is a windowed (LiF) beam port (U9A) at the Brookhaven National Laboratory, National Synchrotron Light Source (NSLS), with a storage ring design. The light is dispersed by a 0.5-m monochromator typically using 1-mm slits and 2-nm resolution. A stainless steel cell with LiF windows is used as the sample cell. Photoproduct emission is detected at right angles with an Acton 0.2-m monochromator and a cooled RCA C31034 A02 photomultiplier tube (PMT). The spectral detection efficiency is calibrated by turning the excitation monochromator to zeroth order using the synchrotron radiation as a white light source. The signal from the PMT is then sent to a NIM photon counting electronics in conjunction with a LeCroy 3500 multichannel analyzer for data acquisition. Since the NSLS produces light pulses at a repetition rate of 6.5 MHz (working as a one-bunch mode), a maximum time window of approximately 150 ns is available for time decay measurement. This makes long emission decay difficult to determine. The sample gas pressure is monitored using a 1-torr MKS Barocell head.

The apparatus for generating coherent vuv sources using harmonic generation in rare gases is shown in Fig. 1. A Nd:YAG laser is frequency doubled to 532 nm and used to pump a dye laser using Rhodamine (Exciton, Inc.) dyes. The dye laser output of 40-70 mJ/pulse at the 555-600 nm region is mixed with residual 1.06-μm light from the YAG laser to typically produce 5-10 mJ of 365-385-nm light. Experiments are also performed using the third harmonic of the YAG laser at 355 nm. The mixing KDP crystal is angle-tuned by a feedback controlled system that allows the scanning of excitation wavelength.

In the lower half of Fig. 1, the device is shown to have three chambers specifically for the generation, utilization, and detection of the vuv light. It is 76 cm long and constructed of standard 2.75-in. conflat vacuum hardware. A 10-cm f.l. lens is used to focus the near uv light into the third harmonic generation (THG) section. A LiF lens (10 cm f.l. at 400 nm) is placed between the THG section and the sample section. A LiF window is used to separate the sample cell from the nitric oxide ionization cell, which is used as a vuv detector with 200-300 V bias across the plates (2.5 cm apart). The THG cell is filled with different mixtures of rare gases (Ar, Kr, and Xe) depending on the desired excitation wavelengths. Pressure in the THG cell is monitored using a Wallace and Tiernan 800 torr sensor head. Pressure in the sample cell is measured using a Hastings thermocouple gauge and 1-torr MKS Baratron head. The acetylene is passed through a trap at 195 K before use. The other gases are passed through traps at either 77 K or 195 K, as appropriate.

Because the THG process is only typically reported at 10^{-6} efficient, near uv scattered light is expected to be large compared to the desired signal, the photoproduct luminescence resulting from vuv photolysis. The sample chamber is painted black with Aquadag and a number of black anodized aluminum baffles are inserted along the beam path. A liquid filter consisting of 5-g/ℓ hydrated $Fe_2(SO_4)_3$ is used in the right angle detection system. The filter transmits emission from 400 nm to 940 nm with a transmission dip from 550 nm to 620 nm while blocking scattered light. The liquid filter produces virtually no fluorescence and has two orders of magnitude more attenuation than a glass color filter. A Hammamatsu R955 PMT that is gated on by a voltage pulse with a variable delay time is used for observing the emission. The output of the PMT is amplified 100 times and sends to either a PAR boxcar or a transient digitizer/minicomputer system for signal averaging and data reduction. In some experiments, a pinhole (~0.3 mm in diameter) is inserted into the midsection of the sample chamber. Because of the very large difference in the refractive index of the LiF lens (for example, n = 1.62 @ 122 nm and n = 1.40 @ 366 nm), the vuv and near uv laser beams are focused at very different focal lengths. This allows the pinhole to discriminate much of the near uv light. A better-than-two orders of magnitude of reduction in the scattered light is attained.

Results

Initial survey data are obtained using the synchrotron. The photofragment emission spectrum obtained using an acetylene pressure of 40 mtorr is shown in Fig. 2. This spectrum is acquired by scanning the emission monochromator while holding the excitation monochromator fixed at 120 nm. A monochromator resolution of 20 nm is used in order to maximize the instrumental throughput. Even so, there is still a significant amount of noise shown in the spectrum and no detectable structure is identified. Previous observations at higher resolution (1 nm) also show *no* significant structure.[7,9,10] However, the observed spectrum differs from the previous work in that it shows emission extending farther to the red (essentially to the cut-off wavelength of the PMT, 900 nm). This is due to the broader spectral response of the PMT's used in the present work.

Figure 3 shows the synchrotron excitation spectrum, and the laser absorption and excitation spectra. The excitation spectra are produced by scanning the excitation wavelength and monitoring the photoproduct emission using a bandpass filter. The absorption spectrum is created by monitoring the output of the NO ionization cell in Fig. 1 while scanning the dye laser. The wavelength resolution in the laser experiments is given by $\sqrt{3}$ times the Nd:YAG laser bandwidth *or* approximately 2 cm^{-1} in the vuv.

The synchrotron excitation spectrum shows peaks due to a combination of vibrational progression in Rydberg states and valence states. The spectrum agrees with the previous work,[10] which indicates a cut-off wavelength of emission at 136.5 nm, rather than 130 nm.[7] The high-resolution laser spectra are scans of one vibronic band. The transition is assigned as a member of the R Rydberg series, n = 4, $v_2' = 1$ with vibronic symmetry $^1\Pi_u \longleftarrow {}^1\Sigma^+{}_g$. Previous absorption measurements place the transition at 1220.63 Å. The most notable observation on comparison of the laser excitation spectrum and the laser absorption spectrum is their similarity. Although individual rotational lines are not resolved because their spacing $2B_v$ is about equal to the laser bandwidth, the similarity in rotational contours suggests that the predissociation process leading to the emitting photofragment is independent of J; i.e., a homogeneous predissociation rather than proportional to J(J + 1) as in a heterogeneous process.[25]

The excitation spectra are also taken at different emission wavelength regions. Figures 4 and 5 depict two spectra obtained with narrow band pass filters centered at 440 nm and 850 nm. One interesting feature is the distinct shift in the amplitudes of vibronic peaks in the two spectra. It indicates that the higher the excitation photon energy the higher the emitting photon energy; i.e., the excitation energy in the C_2H^* photofragments is directly correlated to that of the C_2H_2 precursors.

The temporal behavior of the emissions is investigated in detail. Fluorescence signal is averaged over a large number of shots (>1000) for a particular gas mixture of acetylene. The difference between this averaged signal and the background (an averaged signal with the cell empty) is then fit to an exponential over the temporal region where the background intensity is small compared to the signal. It appears that single exponential decays give good fits to curves for various pressures of acetylene/quencher mixtures. The decay rate constants are plotted in Fig. 6 for 10 mtorr of acetylene versus pressures of itself, Xe, and He. Using a simple linear fit for each of the added gas pressures, a bimolecular rate constant can be derived by calculating the slope of the linear curve. The quenching rate constants of the C_2H^* emission for all the gases studied are summarized in Table I. It should be noted, however, that the rate constants are somewhat phenomenological in the sense that we are observing decay of emission over a broad spectral region, rather than a state-selected decay.

Collision-free fluorescence lifetimes of the emission are also determined at different excitation wavelengths (see Table II). This is derived by extrapolating the C_2H^* photoemission quenching curve of C_2H_2 to zero pressure. The values are in good agreement with the previous works.[9,10] However, the result seems to indicate that at a shorter excitation wavelength a shorter emission lifetime is obtained. This is consistent with the observation that the shorter wavelength C_2H^* emitters tend to be more short-lived, since it is also observed that the shorter wavelength excitation leads to more excited photoproducts.

Additional experiments are implemented on the C_2D_2 molecule. It is determined that similar quenching rate constants and lifetimes are measured for the excited C_2D photofragment. However, the collision-free lifetime of the C_2D emission is measured to be longer (~10 μs) when an excitation wavelength of 1222.6 Å corresponding a 4R Rydberg transition for $\nu_2' = 1$ is used. This may have some implication as to the electronic and vibrational coupling between the electronic manifolds.

Discussion

It is interesting to examine the quenching rate constants for the various species shown in Table I. A comparison with triplet state quenching of other Π electron systems in rare gas matrices[26] indicates that triplet state quenching in the present system cannot be invoked. For example, it has been observed that the quenching of the triplet state lifetime of benzene varied by a factor

>100 in the series of Ar, Kr, and Xe quenching gases. If triplet quenching were the process occurring in the acetylene/C_2H system, then a much larger change of quenching cross sections in the He, Ar, Kr, and Xe series would be expected. Furthermore, the existence of low-lying singlet states of O_2 would be expected to rapidly quench a triplet state by spin exchange. Thus, the quenching data summarized in Table I implies that neither a metastable precursor of the photochemical emitter nor the emitter itself are triplet states, as had been previously suggested.[14] We may also exclude other spin orbit coupled intersystem emission processes such as a quartet state to doublet state transition in the C_2H^* which has been proposed[4] as a component of the visible luminescence.

As mentioned before, the similarity in the rotational contour between the fluorescence excitation and the absorption spectra can be interpreted to mean that the predissociation of C_2H_2 is caused by a homogeneous perturbation. Since the excited C_2H_2 state symmetry is $^1\Pi_u$, the exit channel of the predissociation must also be $^1\Pi_u$; the H atom is ^2S, so the C_2H^* must be produced in states correlating with Π electronic symmetry. By examining the C_2H electronic state calculation of Shih et al.,[4] it is believed that $3^2A'$ is the most likely candidate emitting state of C_2H on the basis of energy spacing correlates with $^2\Pi$ at its equilibrium C-C bond spacing. However, our lifetime measurements are not in agreement with the calculated value (~0.2 μs) for this particular state.[4] It is not clear whether the considerable discrepancy is due to the imprecision of the theoretical model in determining transition strength.

It is appropriate to compare the present quenching studies with rates that have been previously measured. Becker et al.[9] measured rates for H_2, N_2, and Ar quenching that are approximately 1.5 to 2 times faster than ours, while their rate for C_2H_2 quenching is identical to ours, and also to that measured by Saito et al.[10] Saito's rate for He quenching is slightly faster. Saito et al. measured rates at several emission wavelengths and found that the rates increase at shorter wavelengths, consistent with the idea that short wavelength emission represents more highly excited molecules. Shokoohi et al.[27] measure longer lifetimes and slower quenching rates in the near infrared emission of C_2H^*, but these processes may represent quenching that is more like vibrational relaxation than electronic relaxation due to the complex perturbations in the low-lying electronic states of C_2H.[4,5] Suto et al.[23] in nontime-resolved quenching studies have measured a product of quench rate times decay time for Ar, N_2, and C_2H_2. However, their values for this product are a factor of two higher than the values measured by Saito et al.,[10] Becker et al.,[9] or our work. Furthermore, Suto et al. report a dramatic decrease in the values of this product at shorter wavelengths which we do not observe in comparing our data at 118 nm and 122 nm.

In conclusion, by using two novel tunable vuv sources, a synchrotron light source and a frequency tripled laser, we have measured time-resolved quenching rate for the C_2H^* and C_2D^* photoproducts by a number of gas species. In addition, collision-free lifetimes of the C_2H^* and C_2D^* emission are measured at different excitation wavelengths. One of the emitting states is tentatively assigned to be the $3^2A'$ state. The results indicate that a metastable triplet intermediate does not play a significant role in the formation of the observed emission.

Acknowledgment

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References

1. S. J. Harris, "The Chemistry of Combustion Processes," T. M. Sloane, ed. (Amer. Chem. Soc., Washington, 1984). p. 23.

2. S. S. Prasad and W. T. Huntress, Jr., Astrophys. J. 239, 151 (1980).

3. A. H. Laufer and R. Lechleider, J. Phs. Chem. 88, 63 (1984).

4. S. K. Shih, S. D. Peyerimhoff, and R. J. Buenker, J. Mol. Spectros. 74, 124 (1979).

5. P. G. Carrick, A. J. Merer, and R. F. Curl, Jr., J. Chem. Phys. 78, 3652 (1983).

6. H. Okabe, Photochemistry of Small Molecules, (Wiley, New York, 1978) p. 262.

7. H. Okabe, J. Chem. Phys. 62, 2782 (1975).

8. H. Okabe, J. Chem. Phys. 75, 2772 (1981).

9. H. Becker, D. Haaks, and M. Schurgers, Z. Naturforsch, 26a, 1770 (1971).

10. Y. Saito, T. Hikida, T. Ichimura, and Y. Mori, J. Chem. Phys. 80, 31 (1984)

11. J. R. McDonald, A. P. Baronavski, and V. M. Donnelly, Chem. Phys. 33, 161 (1978).

12. W. R. M. Graham, K. I. Dismuke, and W. Weltner, Jr., J. Chem. Phys. 60, 3817 (1974).

13. A. H. Laufer, J. Chem. Phys. 73, 49 (1980).

14. A. H. Laufer and Y. L. Yung, J. Phys. Chem. 87, 181 (1983).

15. Y. Osamura and H. F. Schaefer III, Chem. Phys. Lett. 79, 412 (1981).

16. R. Krishnan, M. J. Frisch, J. A. Pople, and P. Von R. Schleyer, Chem. Phys. Lett. 79, 408 (1981).

17. K. A. White and G. C. Schatz, J. Phys. Chem. 88, 2049 (1984).

18. J. C. Miller, R. N. Compton, and C. D. Cooper, J. Chem. Phys. 76, 3967 (1982).

19. R. Mahon, T. J. McIlrath, and D. W. Koopman, Appl. Phys. Lett. 33, 305 (1978); R. Mahon, T. J. McIlrath, V. P. Myerscough, and D. W. Koopman, IEEE J. Quant. Electron. 15, 444 (1979).

20. T. J. McIlrath and R. R. Freeman, Laser Techniques for Extreme Ultraviolet Spectroscopy, (American Inst. of Physics New York, 1982).

21. R. Hilbig and R. Wallenstein, IEEE. J. Quantum Electron 17, 1566 (1981).

22. A. H. Kung, Opt. Lett. 8, 24 (1983).

23. M. Suto and L. C. Lee, J. Chem. Phys. 80, 4824 (1984).

24. J. Tellinghuisen, J. Chem. Phys. 57, 2397 (1972).

25. P. B. Sackett, Appl. Opt. 11, 2181 (1972).

26. S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," (Prentice-Hall, Inc., Englewood Cliffs, NJ, 1969) p. 312.

27. F. Shokoohi, T. A. Watson, H. Reisler, A. M. Renlund, and C. Wittig, to be published.

TABLE I

QUENCHING RATE CONSTANTS OF C_2H EMISSION BY A NUMBER OF SPECIES

	Rate Constants (sec^{-1} $torr^{-1}$)
O_2	$1.43 \pm 0.26 \times 10^6$
Ar	$7.7 \pm 1.1 \times 10^5$
N_2	$9.8 \pm 0.71 \times 10^5$
Kr	$6.25 \pm 0.35 \times 10^5$
Xe	$1.30 \pm 0.04 \times 10^6$
H_2	$1.65 \pm 0.04 \times 10^6$
D_2	$1.36 \pm 0.08 \times 10^6$
CO	$1.39 \pm 0.9 \times 10^6$
He	$4.71 \pm 0.08 \times 10^5$
(1220 Å) C_2H_2	$5.03 \pm 0.15 \times 10^6$
(1182 Å) C_2H_2)	$4.79 \pm 0.15 \times 10^6$

TABLE II

COLLISION-FREE LIFETIMES OF C_2H EMISSION AT DIFFERENT EXCITATION WAVELENGTHS

Wavelength (nm)	Electronic State of C_2H_2	Lifetime (μs)
118.22	$4R', \nu_2' = 1$	6.1 ± 0.5
122.02	$4R, \nu_2' = 1$	6.6 ± 0.5
128.19	$3R''', \nu_2' = 2$	8.8 ± 0.8

Figure Captions

1. A schematic diagram of the experimental apparatus.
2. An emission spectrum of C_2H^* observed with an excitation wavelength of 120 nm.
3. A composite of a synchrotron fluorescence excitation spectrum, a vuv laser absorption spectrum, and a vuv laser fluorescence excitation spectrum.
4. A fluorescence excitation spectrum of C_2H_2 obtained with a 440-nm band-pass filter.
5. A fluorescence excitation spectrum of C_2H_2 obtained with a 850-nm band-pass filter.
6. A plot of the inverse of the fluorescence lifetime as a function of the quenching gas pressure.

APPARATUS FOR VACUUM ULTRAVIOLET PHOTOLYSIS

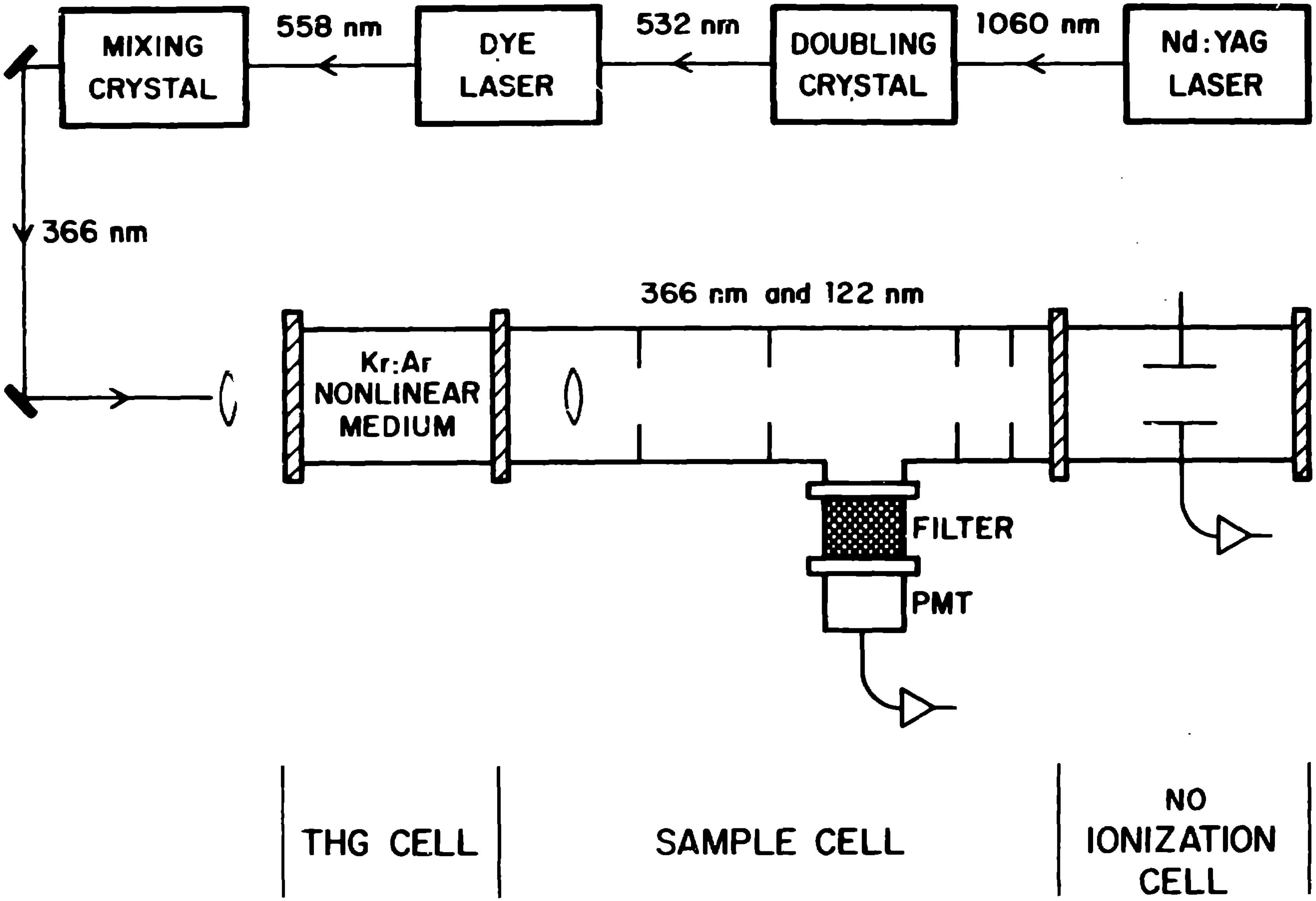

Figure 1

CHM-VG-5430

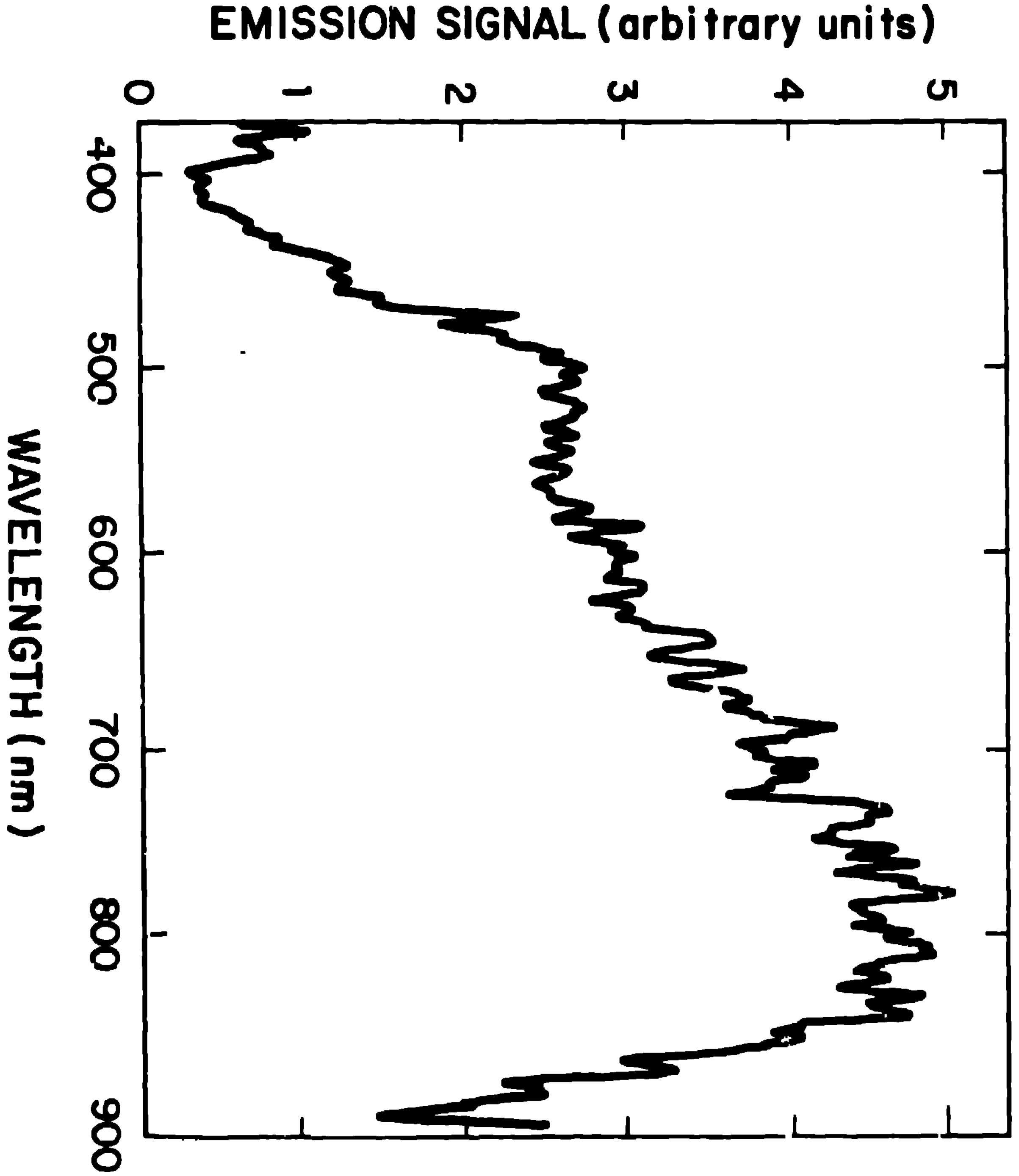
EMISSION SIGNAL (arbitrary units)
0
1
2
3
4
5
400
500
600
700
800
900
WAVELENGTH (nm)

Figure 2

A COMPARISON OF A SYNCHROTRON SPECTRUM AND THE RESOLUTION AVAILABLE FROM A LASER SOURCE

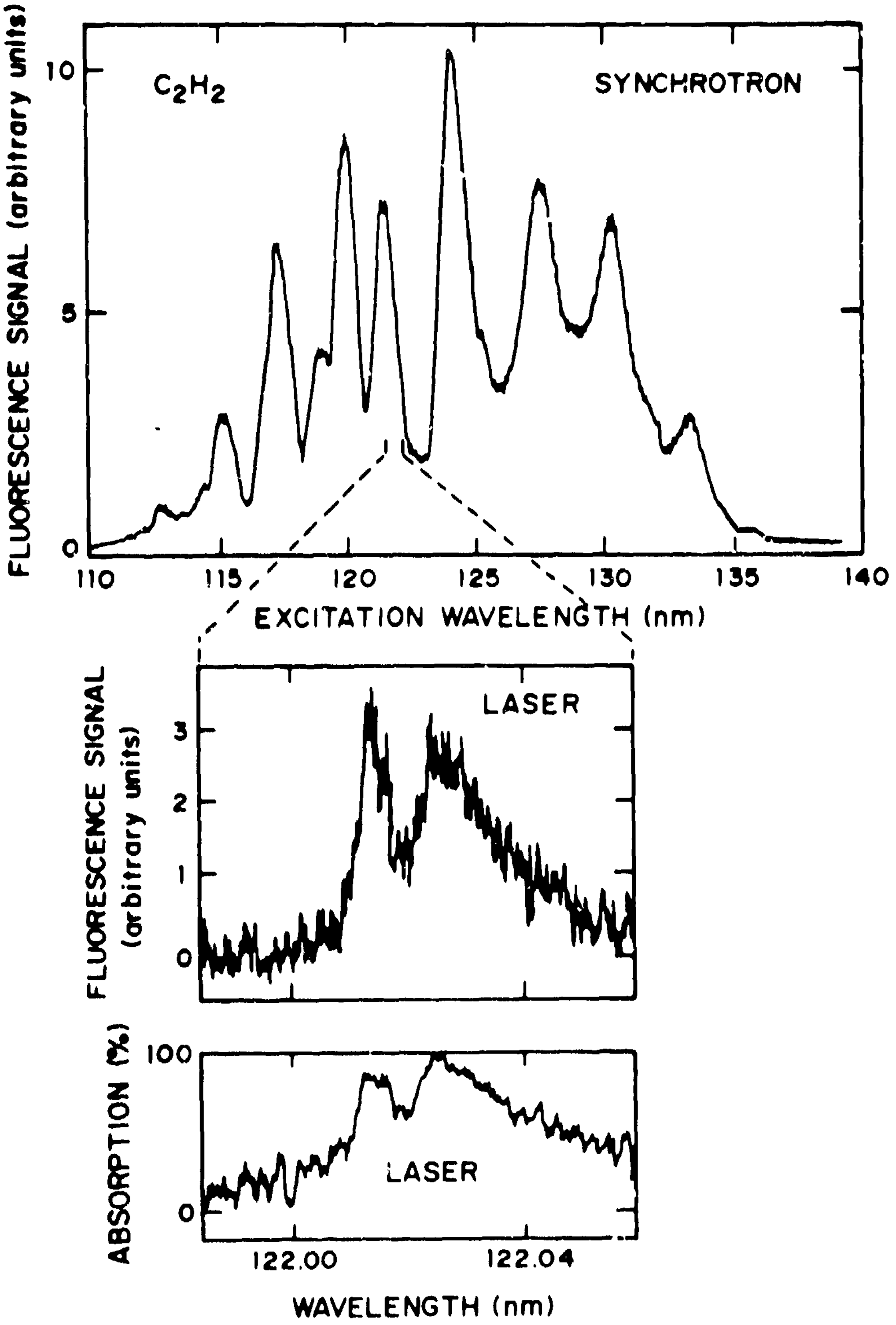

Figure 3

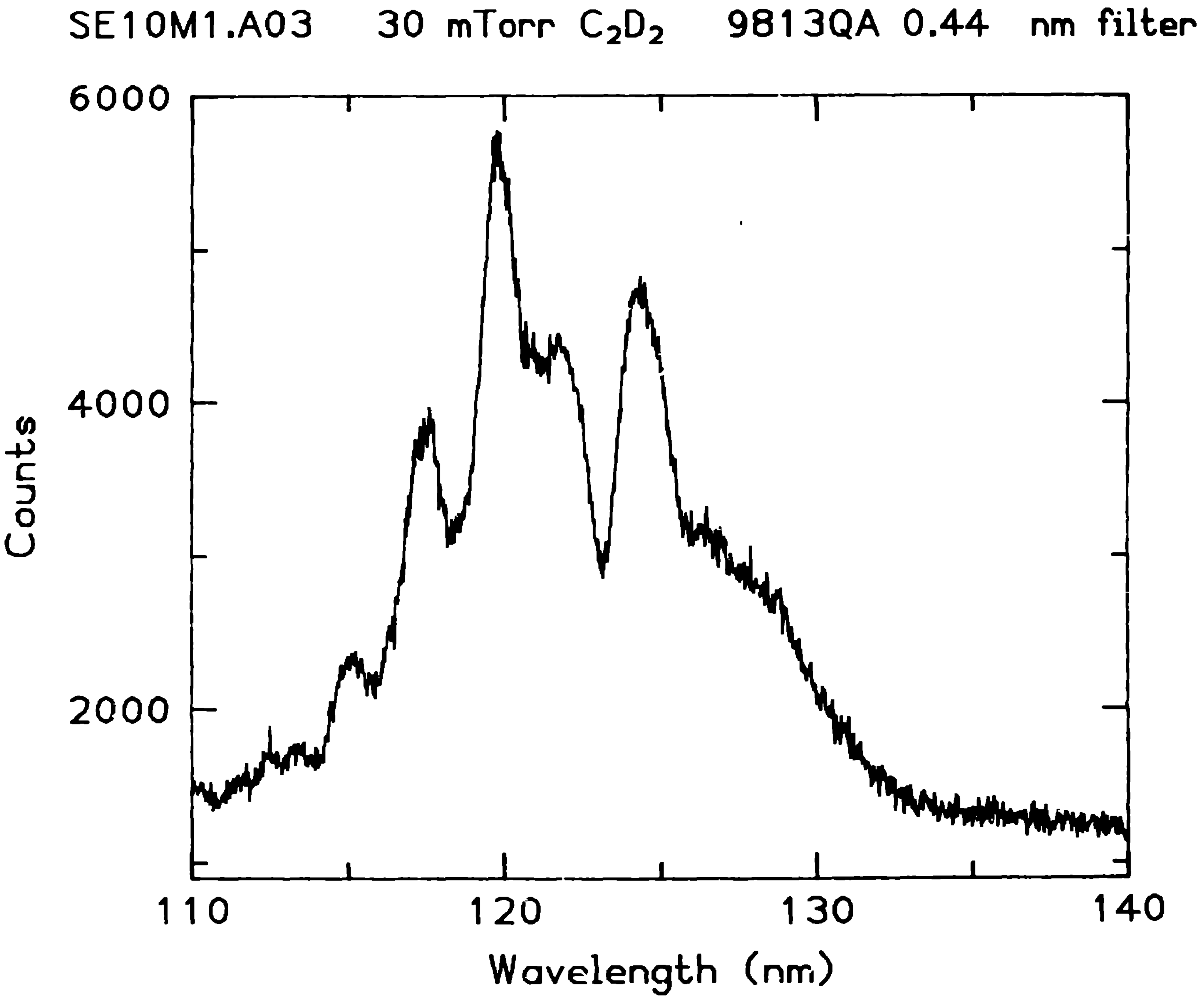
SE10M1.A03 30 mTorr C_2D_2 9813QA 0.44 nm filter
6000
4000
2000
Counts
110
120
130
140
Wavelength (nm)

Figure 4

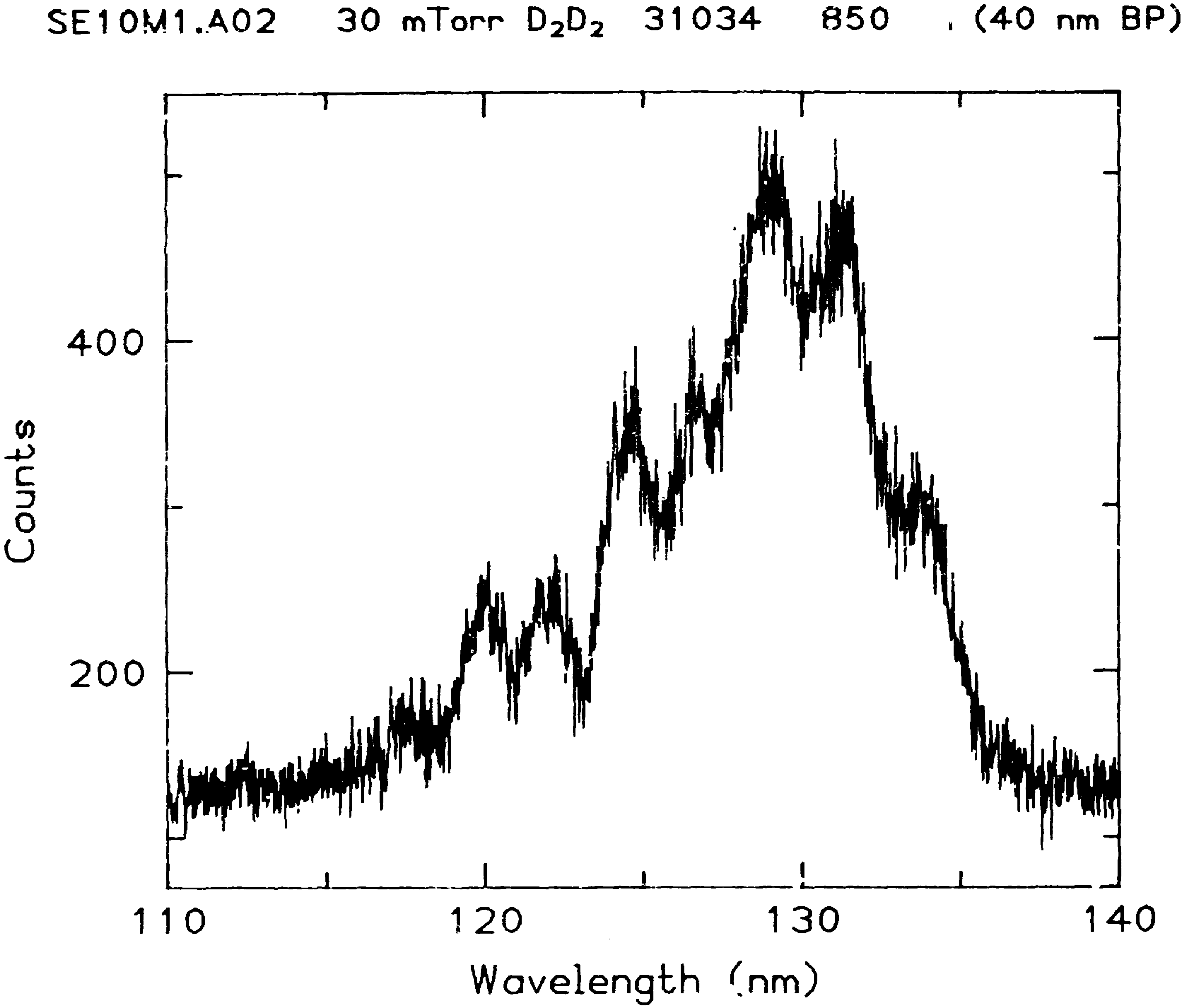
SE10M1.A02 30 mTorr D_2D_2 31034 850 . (40 nm BP)
Counts
400
200
110
120
130
140
Wavelength (nm)

Figure 5

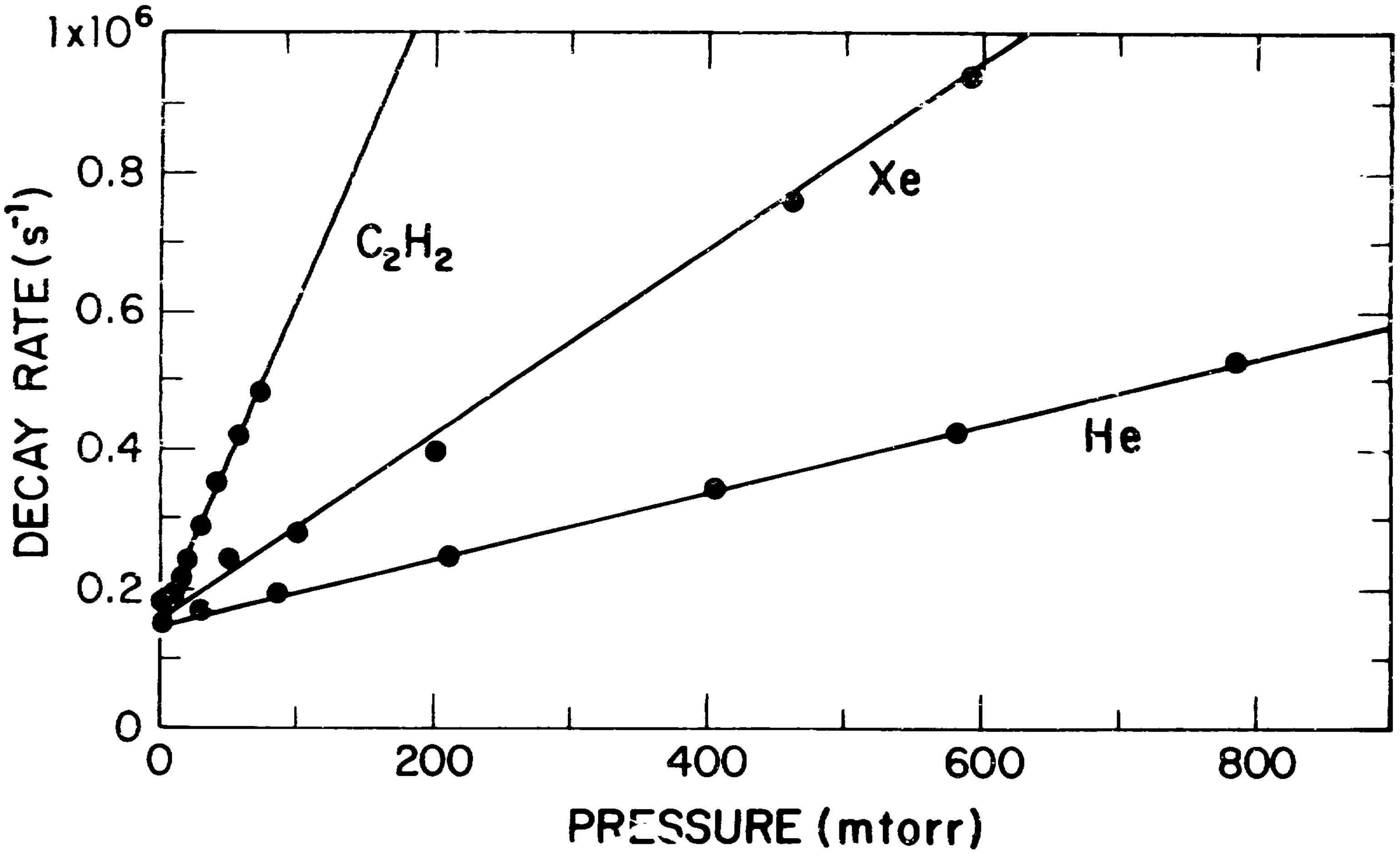

Figure 6

CHM-VG-5915