

Short Communication

Extinction coefficients of azomethane and dimethyl mercury in the near ultra-violet

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Azomethane and dimethyl mercury have been extensively used as photochemical sources of methyl radicals. Accurate values of the extinction coefficients for dimethyl mercury have not hitherto been available; for azomethane, values at wavelengths greater than 210 nm in both gas phase and solution have been measured previously¹. The azomethane absorption in this region is rather weak and continuous with a maximum at approximately 340 nm. A single study of the electronic spectrum below 210 nm has been reported². Dimethyl mercury is reported³ to have a diffuse banded spectrum with a vibrational spacing of the order of 350 cm^{-1} superimposed on a continuum. To aid in elucidating the photochemistry of these systems, we have measured the extinction coefficients of these molecules in the region from 170 nm to 360 nm.

Experimental

Absorption measurements were made by use of a 0.75 m Fastie-Ebert monochromator. The spectral resolution of the instrument, with a 2400 grooves per mm grating and $10\ \mu\text{m}$ slits is about 0.005 nm. The molecular hydrogen continuum served as the background for the wavelength range 170–360 nm. A stainless-steel absorption cell (15.02 cm long) was placed at the exit slit of the monochromator. The vacuum system to which the cell was attached maintained a pressure of less than 10^{-5} Torr. It also was fabricated of stainless steel to minimize any gas–solid interaction. Gas pressures were measured with a capacitance manometer. The maximum error associated with the pressure measurement was 1.5% in the pressure region around 350 mTorr.

Light intensities were measured by a 13-stage photomultiplier tube (PMT). The output signal from the PMT was fed into a photon-counting system of commercially available modules consisting of several stages of amplification, a discriminator, and a scaler. Signals were obtained for preset times to minimize the statistical error in the count rate, and fed into a paper tape punch. The monochromator wavelength drive was connected to a stepping motor which could be preset to advance the number of steps desired. The actual number of steps was monitored

with a scaler; the latter was also connected to the tape punch. In a typical scan, the wavelength drive was manually adjusted to the initial value and the number of steps required to achieve the desired wavelength increment was programmed into the stepping motor index. After the appropriate counting interval was adjusted to minimize statistical fluctuations, the data were dumped into the punch; the photon-counting scaler and timer were gated "off" and the stepping motor was moved the requisite number of steps after which the gating signal was removed and counting continued. The punched paper tape data were computer-reduced and ultimately plotted by computer.

Since this apparatus operates in the "single-beam" mode, it was necessary to record the radiation transmitted through the cell for "sample in, I " and "sample out, I_0 ". To take account of the effect of drift in the incident light intensity, I_0 was scanned both before the cell was filled and after the absorbing material was pumped away. The two values differed by 5% or less and were averaged to obtain the "true" I_0 . Short term fluctuations were insignificant.

Both the dimethyl mercury and azomethane were obtained commercially and used without further purification. In each case, the material was >99% pure according to the manufacturer. Each was thoroughly degassed prior to use. Hydrocarbon impurities, if present, did not exceed 0.1% as determined by flame-ionization gas chromatography.

Results and discussion

Extinction coefficients, ϵ , are defined by the relation:

$$I/I_0 = \exp(-\epsilon px)$$

where I and I_0 are the transmitted and incident light intensities, p is the pressure in atmospheres at 273 K, and x is the path length in cm. The data represent averages of several runs at each wavelength and the spread of points about the curve was, in all cases, less than $\pm 10\%$.

Azomethane

The azomethane absorption spectrum is shown in Fig. 1. In the wavelength region between 170 nm and 210 nm, values were obtained at 0.05 nm intervals. At longer wavelengths the intervals were 0.2 nm. The spectrum exhibits a very strong continuum with some superimposed structure. The positions of the maxima form a progression as indicated in Table 1, which also shows the differences between adjacent bands.

A recent investigation of the Raman and infra-red spectra of azomethane⁴ has resulted in the assignment of the observed absorption at 584 cm^{-1} to the CNN bending fundamental in the ground electronic state. We suggest that the observed vibrational sequence in the ultra-violet absorption corresponds to the CNN bending mode in the upper electronic state with a slightly reduced frequency

of 470 cm^{-1} . The underlying electronic absorption has been identified² as an $n_+ \rightarrow \sigma^*$ transition.

The maximum extinction coefficient is at 185.0 nm, where ϵ has a value of $833 \text{ cm}^{-1} \text{ atm}^{-1}$. At wavelengths greater than 220 nm, the absorption is smaller than $1 \text{ cm}^{-1} \text{ atm}^{-1}$ and our values for ϵ are in good agreement with the previously published gas-phase work^{1a,d}.

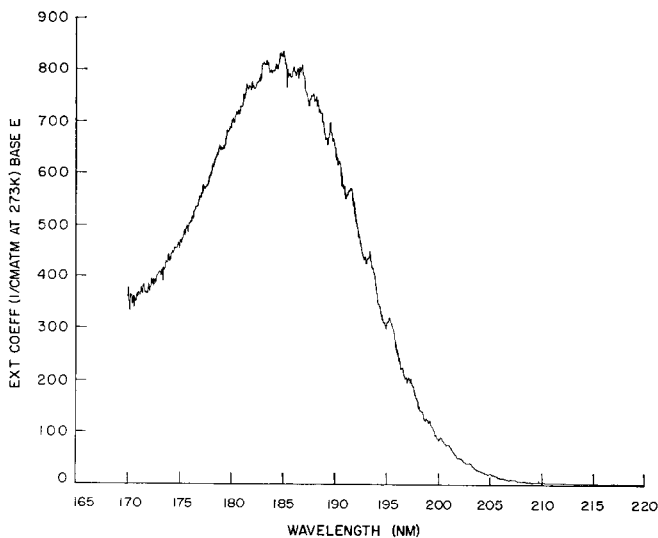


Fig. 1. Absorption spectrum of azomethane between 170 and 220 nm.

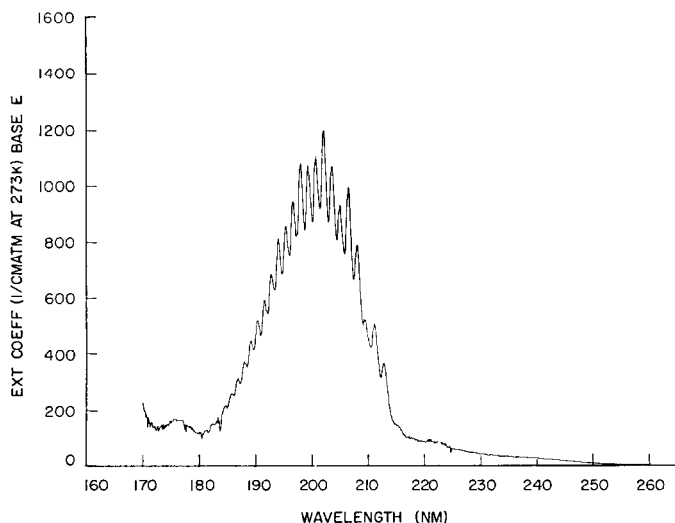


Fig. 2. Absorption spectrum of dimethyl mercury between 170 and 260 nm.

TABLE I

ABSORPTION MAXIMA IN THE ULTRA-VIOLET SPECTRUM OF AZOMETHANE

λ (nm)	ϵ (cm ⁻¹ atm ⁻¹)	$\bar{\nu}$ (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)
175.75	500.2	56,899	497
177.30	576.7	56,402	515
178.90	652.9	55,897	495
180.50	719.4	55,402	381
181.75	770.3	55,021	495
183.40	817.6	54,526	399
184.75	832.9	54,127	364
186.00	806.3	53,763	230
186.80	809.2	53,533	313
187.90	754.6	53,220	463
189.50	687.1	52,757	538
191.50	570.5	52,219	499
193.35	448.7	51,720	504
195.25	321.2	51,216	493
197.15	206.0	50,723	522
199.20	122.8	50,201	450
201.00	75.9	49,751	502
203.05	41.1	49,249	492
205.10	20.2	48,757	448
207.00	9.6	48,309	

Dimethyl mercury

The measured absorption spectrum of dimethyl mercury is shown in Fig. 2. In this case, the spectrum was measured at intervals of 0.08 nm between 170 nm and 270 nm. At $\lambda > 270$ nm, the intervals were 0.2 nm. As is clear, there is a rather long progression beginning at about 184.5 nm and consisting of 23 members; the average spacing between adjacent bands is 347 cm⁻¹. The wavelengths of the absorption maxima are indicated in Table 2. The values agree with the data of

TABLE 2

ABSORPTION MAXIMA IN THE ULTRA-VIOLET SPECTRUM OF DIMETHYL MERCURY

Ref. 3a	Ref. 3b	This work			
		λ (nm)	ϵ (cm ⁻¹ atm ⁻¹)	ν (cm ⁻¹)	$\Delta\nu$ (cm ⁻¹)
		184.56	218.4	54,183	
					327
		185.68	258.5	53,856	
					346
		186.88	316.3	53,510	
					319
		188.00	372.5	53,191	
					315
		189.12	449.5	52,876	
					355
		190.40	522.5	52,521	
					307
		191.52	592.3	52,214	
					347
		192.80	683.9	51,867	
					342
		194.08	815.2	51,525	
					337
		195.36	859.2	51,188	
					334
196.5		196.64	949.6	50,854	
					369
197.8		198.08	1083.7	50,485	
					325
199.0		199.36	1079.2	50,160	
					359
200.5		200.80	1108.9	49,801	
					335
202.0		202.16	1198.6	49,466	
					350
203.2		203.60	1074.4	49,116	
					336
204.7	204.9	205.04	933.8	48,780	
					368
206.2	206.1	206.56	998.1	48,412	
					354
207.8	207.8	208.08	790.9	48,058	
					312
209.3	209.2	209.44	517.2	47,746	
					380
210.9	210.8	211.12	508.2	47,366	
					374
212.5	212.5	212.80	367.3	46,992	
					437
	214.8	214.80	153.5	46,555	

Terenin^{3a} and Thompson^{3b} in the region of overlap, and we have extended the measurements to shorter wavelengths. Assignments of the ground state vibrational frequencies have been made by Gutowsky⁵. The fundamental at 515 cm^{-1} has been unambiguously attributed to a symmetrical stretch. The vibration, 347 cm^{-1} , observed superimposed upon the broad electronic absorption between 184.5–215.0 nm, may be interpreted as the symmetric stretching vibration in the upper electronic state.

At the photochemically important wavelength of 253.7 nm, the extinction coefficient is $2.1\text{ cm}^{-1}\text{ atm}^{-1}$. At all wavelengths between 270 nm and 330 nm, the value of $\epsilon \leq 0.2\text{ cm}^{-1}\text{ atm}^{-1}$.

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