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ULTRAVIOLET ABSORPTION SPECTRUM OF MERCURY IN LOW TEMPERATURE MATRICES

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May, 1965

Ultraviolet Absorption Spectrum of Mercury in Low Temperature Matrices

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ABSTRACT

The u.v. absorption spectrum of mercury ($^3P_1 \leftarrow {}^1S_0$) in Xe, Kr, and Ar matrices has been investigated previously by other workers. The present study verifies the previously published results, extends the investigation to include Ne, N_2 and O_2 matrices, and analyzes the effects of changing the temperature of the matrix and the concentration of mercury in the matrix. With respect to the gas phase transition at 2537Å, in Ne, Ar, Kr, Xe, and N_2 the observed absorptions are shifted to shorter wave length by 940, 1270, 775, 10, and 845 cm^{-1}, respectively. The half-widths of the absorptions increase with increasing temperature and with increasing mercury concentration. Xe and Kr matrices show partially resolved triplets, while N_2 yields a broad doublet. The separate components of the multiplets respond differently upon warming of the matrices. For matrices with a mercury concentration > 1%, additional features, presumably due to dimers or other aggregates, are observed.

INTRODUCTION

Several workers have studied the visible and ultraviolet spectra of various species trapped in inert gas matrices. However, the interpretation of their results has sometimes been complicated by various so-called "matrix effects": shifts from the gas phase position, broadening, and splitting into multiplets.[1] All three of these phenomena are observed in the spectrum of mercury atoms trapped in various matrices. It is therefore appropriate to study this system in detail in the hope that additional insight into the causes can be obtained.

In many respects, the mercury-inert gas system is ideal for study: the vapor phase of mercury consists almost entirely of mercury atoms; the investigation is experimentally straightforward, and only one strong transition is expected to be observed in the spectral region of interest.

The spectrum of the $^3P_1 \leftarrow {}^1S_0$ transition in Xe, Kr, Ar and isopentane has been studied previously by McCarty and Robinson[2,3] and by Roncin and Damany-Astoin;[4] the results are collected in Table I. The $^1P_1 \leftarrow {}^1S_0$ transition has also been studied[4,5] and an absorption attributed to the $^3P_2 \leftarrow {}^1S_0$ transition has been observed.[4]

The present work extends the investigation of the $^3P_1 \leftarrow {}^1S_0$ transition. The main objective was to study the effect of using new matrices, changing target temperature, and varying mercury concentration.

EXPERIMENTAL

The metal cryostat used for these experiments consisted of an outer shell with sapphire windows along the optical axis, and an insert which

contained the refrigerant and from which was suspended the copper block in which the target was mounted. Two different inserts were used, depending on the refrigerant selected; the liquid helium insert, unlike the liquid hydrogen counterpart, had a liquid nitrogen radiation shield which surrounded the liquid helium reservoir and the target. The insert could be turned 90° during the course of the experiment, allowing the target to be oriented normal either to the matrix gas inlet system or to the optical axis. Both sapphire and CsBr were used as target materials.

The liquid hydrogen insert was equipped with a copper-gold (2.1% cobalt) thermocouple for measuring temperatures during warm-up experiments. When the sapphire target was used, the thermocouple was attached to the copper block immediately below the target. The CsBr target, on the other hand, had a thermocouple well bored from the edge to the center of the target; the thermocouple was secured in the target with Wood's metal. It was discovered that, although the thermocouple junction was thus exposed to irradiation by the hydrogen discharge tube while spectra were being taken, this environment did not change the temperature recorded. The thermocouple emf was transmitted directly to a chart recorder, thus allowing a time-temperature history of the sample to be made during a warm-up experiment.

A schematic drawing of the matrix gas inlet system is shown in Figure 1. The inert gas at a pressure of 0.1 to 1.0 Torr partially equilibrated with the mercury vapor above the mercury reservoir, and then passed through the 0.5 mm orifice into the cryostat. A water bath placed around the mercury reservoir controlled the mercury vapor pressure. The total gas pressure above the mercury reservoir was measured with a McCloud gage; except when a measurement was being made, the McCloud gage

was isolated from the rest of the system by a closed stopcock to prevent the gage from functioning as a secondary source of mercury. The inert gas was provided to the inlet system by a dual channel system utilizing Fischer-Porter flow meters to assure reproducible flow rates. The purpose of the second channel was to permit addition of small amounts of impurity gases.

Linde High Purity gases or equivalent were used without further purification. Ballard's C. P. Tripple Distilled mercury was distilled under vacuum into the reservoir in the inlet system.

Spectra were photographed in the region from 2200 to 3000Å with a 0.75 meter Jarrell-Ash f/6.3 spectrograph having a 2160 lines per millimeter grating blazed for 3000Å and giving a dispersion in first order of 5Å/mm. The continuum was provided by a hydrogen discharge tube.

The experimental parameters are summarized in Table II. The values of M/R (moles of Matrix/moles of Radical) were calculated on the assumption that the mercury vapor equilibrates with the inert gas; however, since, particularly at high flow rates, equilibration was incomplete, the calculated values represent only the lower limit of the actual M/R.

With the exception of neon, all matrices were studied both at 4 and at 20°K; neon was deposited at 2 and 4°K. During a typical experiment, between 0.3 and 6 millimoles of matrix were deposited. Prior to the beginning of deposition, the cryostat pressure was less than 4×10^{-6} Torr; during deposition at 20°K, the pressure remained less than 8×10^{-6} Torr. When liquid helium was used as a refrigerant, the pressure increased in some cases to 1×10^{-4} Torr during deposition;

this circumstance is attributable to the small size of the windows in the liquid nitrogen radiation shield and hence to the small cross sectional area available for cryogenic pumping by the liquid helium Dewar. Nevertheless the mean free path was still longer than the actual distance from the inlet system to the target.

Since it was necessary to assure that the observed spectra were due to mercury atoms which were well isolated from one another, a two-fold experimental approach was used. In the majority of experiments, parameters were selected to assure the maximum degree of isolation; in particular, the maximum practical M/R was used and in some instances liquid-helium was used in place of liquid hydrogen. On the other hand, in some experiments the degree of isolation was deliberately reduced so that spectra due to dimers and other aggregates could be more readily identified.

For warm up experiments, the refrigerant was allowed to evaporate and then spectra were periodically photographed as the matrix warmed of its own accord. The rate of warm up was 20°K/min initially and decreased to 4°K/min at 50°K. In some experiments the partially warmed matrix was quenched by the reintroduction of refrigerant.

In the case of the xenon matrix, the effect of adding ten mole percent of water vapor, nitrogen, or oxygen was also investigated. For these experiments, the impurity gas was metered by the second channel of the flow metering system and was mixed with the xenon prior to reaching the matrix gas inlet system.

In a few experiments with xenon and argon, while the matrix was being deposited, a μ-wave discharge was maintained in the matrix gas

inlet system in the zone immediately before the orifice to the cryostat. This environment in no way influenced the spectra observed.

RESULTS

General: When the mercury atoms were well isolated in the matrix only one absorption feature was observed, having, in some matrices, partially resolved structure. In each of the matrices studied, the center of gravity of this absorption was shifted to shorter wavelength with respect to the gas phase $^3P_1 \leftarrow {}^1S_0$ transition at 2536.5Å. The magnitude of the shift was dependent not only on the type of matrix, but also on the temperature at which the matrix was deposited; the observed shift was slightly greater for matrices deposited at 4°K. The half-width of the absorption was likewise a function both of matrix type and of target temperature; for a given M/R, the matrix deposited at the lower temperature yielded a narrower half-width. Typical densitometer tracings of spectra attributed to well-isolated mercury atoms are shown in Figure 2; Table III summarizes the data for these spectra.

If the degree of isolation was somewhat reduced, the absorption broadened, shifting toward the red, and developed a shoulder on the red edge. Under conditions of poor isolation, new absorption maxima were observed.

Xenon: Large M/R experiments conducted at 20°K with xenon yielded an absorption having three partially resolved maxima. The feature was slightly, but clearly, asymmetric, the short wavelength component being the best resolved. The relative intensities of the three absorption maxima were observed to be constant regardless of experimental parameters. The estimated half-width of the individual members of the triplet was

150 cm^{-1}. The observed maxima were not separated symmetrically, however, it was difficult to estimate the actual locations of the three contributing members because of the shift in apparent maxima caused by overlap of the individual components.

The effect of warming the matrix is illustrated by Figure 3 (a). The following facts were noted:

(1) The position of the short wavelength component of the triplet remained constant.

(2) The two long wavelength components shifted to longer wavelength; the shift was approximately a linear function of temperature and amounted to 1.6 $cm^{-1}/°K$.

(3) The relative intensity of the three components remained constant.

(4) The behavior observed during warm up was reversible; when a matrix which had been warmed to 55°K was returned to 20°K, the initial structure and half-width were recovered.

Since it was possible that one or more members of the triplet might be due to the interaction of mercury atoms with impurities in the xenon lattice, the most probable impurities, N_2, O_2 and H_2O, were purposely added to the matrix in some experiments; the results are illustrated by Figure 4. In general, no large effect was observed although the spectra differed in some details from the spectrum attributed to atoms well isolated in pure xenon. In particular it was found that the addition of impurities resulted in (1) shifting of the blue member of the triplet 10 to 20 cm^{-1} to shorter wavelength; (2) increasing of the half width; (3) altering of the relative intensity of the three components, and (4) the appearance of a shoulder on the long wavelength side when H_2O was the impurity.

The effect of reducing the M/R was also investigated; for an M/R less than 100 it was found that the absorption broadened and shifted to the red, that a shoulder appeared on the long-wavelength side, and that the short wavelength component of the triplet shifted about 10 cm^{-1} to shorter wavelength.

The experiments conducted at 4°K were designed to assure maximum isolation; the M/R was selected to be 1000. However, the spectrum obtained was similar in all respects to the spectrum of poorly isolated atoms; in this case the short wavelength component of the triplet was found 20 cm^{-1} to the blue of its expected location. No explanation for this result can be presented.

Krypton: The spectrum attributed to well isolated mercury atoms in a krypton matrix at 20°K appeared to consist of three poorly resolved components; the short wavelength member contributed only a shoulder to the over-all structure and was not clearly resolved, by contrast with the corresponding component in the xenon matrix. However, with this exception, the spectrum was in all respects similar to that observed in xenon. The estimated separation between the components of the triplet was, within experimental error, the same as in the xenon matrix.

The behavior during warm up of the matrix is illustrated by Figure 3 (b). With increasing temperature the two long-wavelength members of the triplet shifted toward longer wavelength; the shift was approximately linear with temperature, 3 $cm^{-1}/°K$. As this shift progressed, the short-wavelength shoulder became more prominent; above 50°K it developed into a well defined band whose position at 40245 cm^{-1} was observed to be independent of temperature. This behavior suggests that this band could well correspond to the short-wavelength component of

the xenon triplet. The evidence would also suggest that this band gives rise to the short-wavelength shoulder observed in the krypton matrix at 20°K. It is noted that the position of the 40245 cm^{-1} band does not coincide with the estimated position of the component giving rise to the short-wavelength shoulder observed at 20°K; this discrepancy might be attributable to an error in the estimation of the location of the component responsible for the shoulder.

For matrices deposited at 4°K, the center of gravity of the absorption spectrum was at 2487.6Å by comparison with 2488.6Å for matrices deposited at 20°K. The structure of the triplet was no better resolved for the 4°K matrices.

Very small M/R matrices yielded spectra having three new absorptions.

(1) An intense band at 2496.5Å which overshadowed the absorption due to isolated atoms.

(2) A broad shoulder on the long-wavelength side of the 2496.5Å band.

(3) A weak, red-degraded band having a maximum at about 2290Å and a half width of about 1500 cm^{-1}.

Argon: Large M/R experiments with argon matrices at 20°K and at 4°K yielded spectra having a general profile which was similar to that obtained with xenon and krypton matrices, but which failed to show any resolved structure.

By reducing the M/R, three additional bands, each having its counterpart in the spectrum of the krypton matrix, could be obtained (see Figure 5).

(1) The intense band at 2473.5Å shown in Figure 5(b) became the dominant feature in the spectrum when a matrix with M/R < 100 was deposited rapidly.

(2) Under the same conditions, a broad shoulder was observed on the long-wavelength side of the 2473.5Å band. When the matrix was formed more slowly, this shoulder developed into the distinct band at 2498.6Å, illustrated by Figure 5(c).

(3) If a very thick matrix was deposited, a weak, red-degraded band having a maximum at about 2260Å was observed.

Neon: The results of experiments with neon matrices are illustrated by Figure 6 and demonstrate that a large M/R can not always assure isolation of the species being studied. Figures 6 (a) and (b) were obtained with an early experimental configuration having a sapphire target with an exposed area of 7.2 cm^2; the band, located at 2502.0Å, had a half-width of 500 cm^{-1}. The appearance of the short-wavelength shoulder in the large M/R experiment (Figure 6 (b)) suggested, however, that the 2502.0Å band could not be attributed to isolated atoms. To test this hypothesis, the experimental configuration was modified: the exposed area was reduced to 2.4 cm^2, and a CsBr target was used; as a consequence of this modification, the contact area between target and target holder was increased. The new configuration yielded a new band at 2477.4Å (Figure 6 (c)), but no trace of the 2502.0Å band. An experiment at 2.0°K yielded the same result. It is believed that, in view of the conditions under which the 2477.4Å band was observed, it is due to well isolated atoms. It is noted that this absorption has a profile distinctly unlike that observed for xenon, krypton, or argon matrices; the neon profile is characteristic of a

singlet, rather than an unresolved triplet.

Nitrogen: The spectrum attributed to atoms isolated in a nitrogen matrix was characterized by an unsymmetric doublet having a narrow band at 2468.4Å and a broad band at longer wavelength. The short-wavelength band appeared to be nearly temperature independent during warm up experiments, as illustrated by Figure 3 (c). The location of the long wavelength maximum, however, was strongly dependent upon temperature; while this latter band shifted only slightly between 20 and 30°K, above 30°K it shifted rapidly toward longer wavelength at a rate of 25 $cm^{-1}/°K$. Unlike the xenon and krypton matrices, in nitrogen the relative intensities of the two bands changed as a function of temperature; the short wavelength band was no longer observable above 50°K, while the long-wavelength band persisted to 60°K. Thus, while the nitrogen spectrum bears some superficial resemblance to the xenon and krypton matrices, there are some notable distinctions in the behavior of the individual components.

Oxygen: Several attempts, both at 20°K and at 4°K were made to isolate Hg atoms in an oxygen matrix. In no case was it possible to obtain a discrete spectrum between 2200 and 5000Å.

DISCUSSION

Xenon, Krypton, and Argon: Large M/R experiments yielded spectra having shifts in good agreement with the data published by McCarty and Robinson for each of these matrices. On the other hand, the spectrum published by Roncin and Damany-Astoin in argon was also approximated

provided a matrix with a small M/R was deposited rapidly; the experimental condition under which this spectrum was obtained suggests that it can not be attributed to isolated atoms.

McCarty and Robinson reported well resolved triplets in all three matrices; the half-width of the individual components was 30 cm^{-1} in xenon and krypton, and larger for argon. By contrast, in the present work, the triplet was only partially resolved in xenon and krypton, and not resolved in argon; further, the estimated half-width of the individual components was 150 cm^{-1}.

The observed shifts satisfy the predictions of theory,[2,6] both with respect to polarizability of the matrix atoms and with respect to the internuclear distance between nearest neighbors; specifically, the most polarizable matrix shows the smallest blue shift, while the "tightest" matrix shows the largest blue shift.

Neon: McCarty and Robinson have quantitatively explained the shift observed in xenon, krypton and argon on the basis of a Lennard-Jones potential between the trapped mercury atom and the rare gas atoms. If it is assumed that the shift observed in neon should continue the trend found in the other three matrices, McCarty and Robinson's calculations can be extended to the neon matrix; using $\sigma = 2.90$, $M = 0.141$ and $N = 0.0206$, the predicted shift is 3600 cm^{-1}, four times the observed shift. Weltner, Walsh and Angell have observed a similar discrepancy in the case of the C_3 molecule trapped in neon.[7]

Contrary to expectation, the shift of the mercury spectrum in neon was even smaller than that observed in argon; thus in neon, even the

qualitative description of interactions breaks down. It must therefore be concluded that the mercury atom cannot occupy a single substitutional site in a neon lattice. Additional evidence of the uniqueness of the neon matrix is supplied by the fact that the profile of the absorption was distinctly different in neon.

The neon matrix can be satisfactorily described as a crystal "fractured" near the site of a mercury atom; alternatively the mercury atom may occupy two or more substitutional sites simultaneously. In either case, the relatively narrow half-width of the absorption suggests that the environment must be highly reproducible throughout the matrix.

Triplet Splitting in Xenon and Krypton. Although the data do not permit a decision as to the cause of the triplet splitting, several factors can be ruled out and some insight into the nature of the interaction can be obtained.

(1) Multiple sites do not cause the different members of the triplet. One arrives at this conclusion by noting that the relative intensities of the three components are not affected by changing M/R, or deposition rate, or by annealing of the matrix.

(2) By the same argument, one can reason that the splitting can not be accounted for by the trapping of two or more different species.

(3) If the presence of impurities were the cause, one would expect much larger changes than are actually observed when 10% of various impurities were added to the matrix gas.

The breaking of orbital degeneracy remains a possible cause of the triplet. The appearance and behavior of the triplet during warm up

experiments suggests that the primary splitting may be into a doublet, while a secondary interaction results in further splitting of the long wavelength component of the original doublet. The potential curve for the excited state leading to the 2528.6Å component closely parallels the potential curve for the ground state, while the potential curves for the 2536 and 2541Å features must have a steeper slope than the ground state curve. Thus small changes in internuclear distance during warm up would lead to shifting of the two long-wavelength components, but not of the 2528.6Å band.

Comparison with Other Spectra: Since the density of the solid can be approached in liquids and high pressure gases, it is of interest to compare the spectra obtained in these two latter media with the spectra observed in the solid; it is recognized that such a comparison is fraught with pitfalls because of the much greater kinetic energy present in liquids and gases and because of the lack of enduring order in these media. Nevertheless some interesting parallels can be drawn.

(1) High Pressure Spectra: The $^3P_1 \leftarrow {}^1S_0$ mercury transition has been observed in the presence of neon,[8] argon,[8,9] krypton,[10] and nitrogen[9] up to 1500 atm, 820 amagats, 190 amagats, and 680 amagats, respectively.

In each case, the principal absorption was observed to broaden and shift as the pressure was increased; at higher densities, one or more satellites appeared on the short wavelength side of the principal absorption and increased in intensity with increasing density. In the cases of argon and nitrogen the densities achieved were about 80% of the density of the solid. The spectra obtained in these media were

quite similar; at the highest pressures studied they consisted of two broad overlapping features, both to the violet of 2537Å.

Roncin and Damany-Astoin[4] have compared the high pressure spectrum in argon with that obtained in a matrix. It is interesting to note that matrix spectrum of well isolated mercury atoms consists of a single broad feature, unlike the high pressure spectrum. On the other hand, small M/R experiments do yield two absorption maxima; this similarity with the high pressure spectra may be only fortuitous; present data are inadequate to decide.

By contrast, the matrix spectrum of well isolated mercury atoms in nitrogen has two broad maxima and thus shows greater similarity to the respective high pressure spectrum. The data of Robin and Vodar[9] suggest that at 820 amagats corresponding to the density of the solid, the two components of the high-pressure spectrum should be at about 2515 and 2460Å.

(2) Liquid Spectra: The $^3P_1 \leftarrow {}^1S_0$ transition has been observed in numerous solvents.[11,12] Typical spectra consist of two components separated by 25 to 40Å. Typically the short wavelength member of the doublet is narrower than the long wavelength member; the center of gravity of the entire absorption is shifted to longer wavelength from 2537Å.

The general shape of the liquid spectra is strikingly similar to matrix spectra obtained in xenon and nitrogen. In each case, the matrix spectrum has a narrow short wavelength component and a broader long wavelength member (having two intensity maxima in the case of xenon).

The spectrum obtained in a partially warmed krypton matrix has the same characteristic.

Molecular Spectra: Small M/R experiments were conducted under conditions favoring the formation in the matrix of Hg_2 and other aggregates; the spectra observed confirm the presence of the dimer. The strong band appearing at 2496.5Å and 2473.5Å in krypton and argon, respectively, corresponds to the 2540Å band of Hg_2. The absorption located approximately 200Å farther to the violet probably corresponds to the

$$^3\Pi_u\,(^3P_2 + {}^1S_0) \longleftarrow {}^1\Sigma_g^+\,(^1S_0 + {}^1S_0)$$

transition located at 2345Å in the gas phase. The 2498.6Å band in argon and the 2502.0Å band in neon are of uncertain origin, but could also be due to the dimer.

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† Captain U.S. Air Force, sponsored by the Air Force Institute of Technology.

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Table I

Absorption Spectrum of the Mercury $^3P_1 \leftarrow {}^1S_0$ Transition in Solid Matrices

Authors	Matrix	Shift from 2536.5Å (cm^{-1})	Half-Width (cm^{-1})
McCarty and Robinson[2,3]	Xenon	30 ± 10	(a)
	Krypton	795 ± 10	(a)
	Argon	1280 ± 15	(a)
Roncin and Damany-Astoin[4]	iso-C_5H_{12}	-355 ± 80	1000
	Argon	910 ± 80	650

(a) In each case the absorption was observed to split into three components; the half-width of the individual components was 30cm^{-1} for xenon and krypton and larger for argon. The separation of the individual components was 120 ± 15 cm^{-1} in each matrix.

Table II

Experimental Parameters

Matrix	M/R	Temperature of Mercury Reservoir (°C)	Rate of Deposit m-mole/hr	Special Experiments
Xexon	10 - 1000	0 - 61	0.2 - 1.8	Warm-up and quench; μ-wave discharge
Krypton	10 - 3700	0 - 58	0.2 - 1.4	Warm-up and quench
Argon	10 - 2500	0 - 55	0.2 - 2.0	μ-wave discharge
Neon	200 - 2000	0 - 22	0.6 - 2.2	
Nitrogen	200 - 3100	0 - 22	0.6 - 1.7	Warm-up

Table III

Absorption Spectrum of the Mercury $^3P_1 \leftarrow {}^1S_0$ Transition in Solid Matrices

Matrix	Center at Half Maximum Intensity (A)	Center at Half Maximum Intensity (cm^{-1})	Shift from 2536.5A (cm^{-1})	Half Width (cm^{-1})	Absorption Maxima (cm^{-1})
Xenon, 20°K	2536.0	39 420	10 ± 15	305	39 341 ± 15 39 418 ± 15 39 536 ± 10
Krypton, 20°K	2488.6	40 171	760 ± 15	365	40 084 ± 25 40 158 ± 25 40 286 ± 25
Krypton, 4°K	2487.6	40 187	775 ± 15	365	-
Argon, 20°K	2458.4	40 665	1255 ± 15	420	40 611 ± 20
Argon, 4°K	2457.3	40 683	1270 ± 15	435	40 641 ± 30
Neon, 4°K	2477.4	40 353	940 ± 15	360	40 335 ± 20
Nitrogen, 20°K	2486.5	40 205	795 ± 15	780	40 104 ± 75 40 500 ± 15
Nitrogen, 4°K	2483.3	40 257	845 ± 20	750	40 104 ± 75 40 510 ± 15

Figures

Figure 1. Matrix Gas Inlet System.

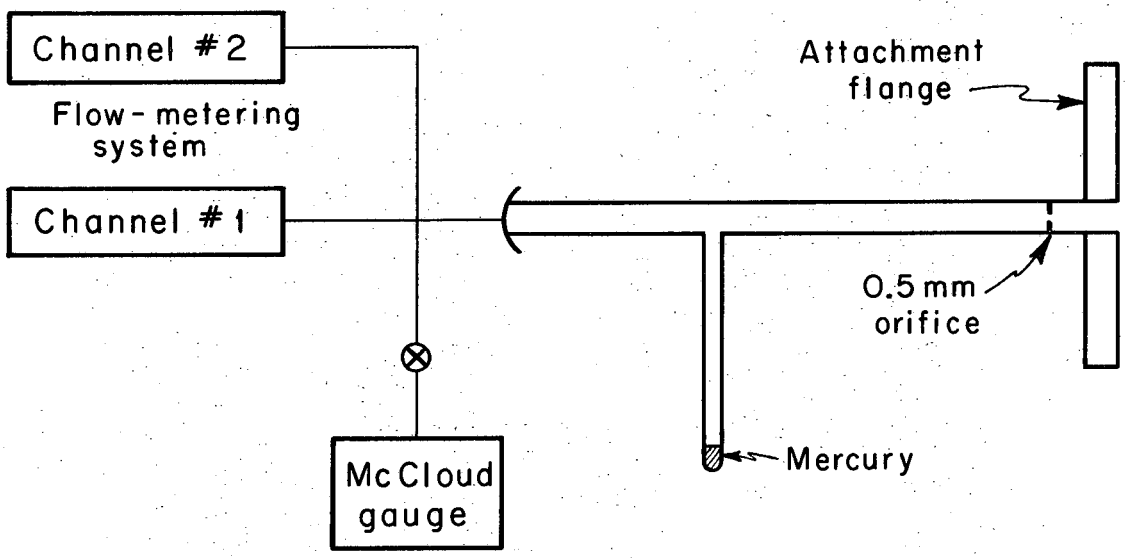
Figure 2. Absorption Spectrum of the Mercury $^3P_1 \leftarrow {}^1S_0$ Transition in Solid Matrices.

Figure 3. Warm-Up Experiments. These Spectra Represent the Behavior over a Temperature Range from 20°K to about 70°K.

Figure 4. Impurity Experiments. Except for the Addition of Different Impurity Gases, the Experimental Parameters were the Same for Each Experiment; $M/R \geq 1000$.

Figure 5. Absorption Spectrum in Argon as a Function of M/R and Deposition Rate.

Figure 6. Absorption Spectrum in Neon. (a) and (b): Sapphire Target with 7.5 cm^2 Exposed Area; (c) CsBr Target with 2.5 cm^2 Exposed Area.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Flow-metering system
Channel #1
McCloud gauge
Attachment flange
0.5 mm orifice
Mercury
MU-35284

Fig. 1

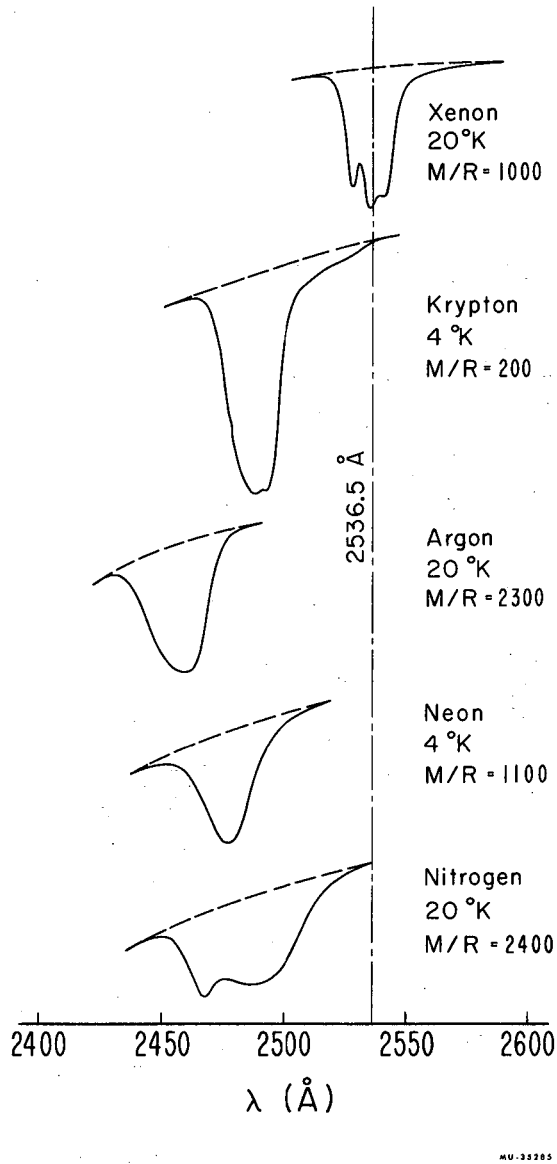
Xenon
20°K
M/R = 1000
Krypton
4 °K
M/R = 200
2536.5 Å
Argon
20 °K
M/R = 2300
Neon
4 °K
M/R = 1100
Nitrogen
20 °K
M/R = 2400
2400
2450
2500
2550
2600
λ (Å)
MU-33285

Fig. 2

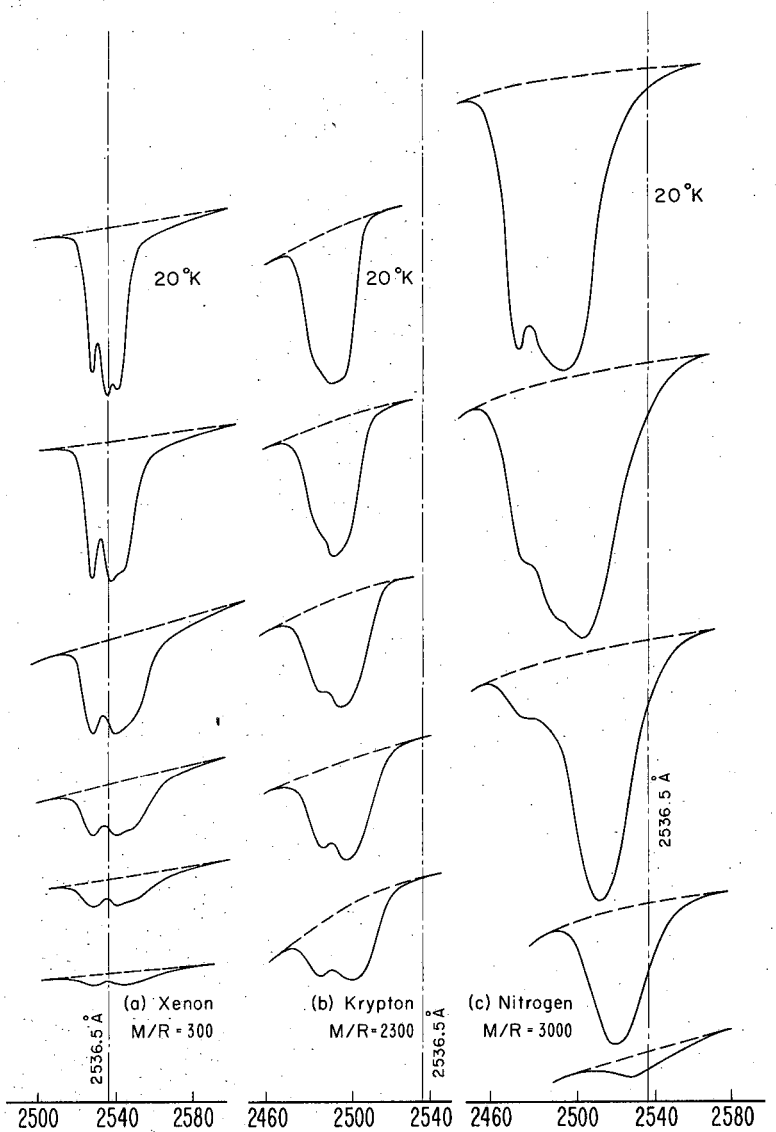
20°K
20°K
20°K
2536.5 Å
(a) Xenon
M/R = 300
2536.5 Å
(b) Krypton
M/R=2300
2536.5 Å
(c) Nitrogen
M/R = 3000
2536.5 Å
2500
2540
2580
2460
2500
2540
2460
2500
2540
2580
λ (Å)

Fig. 3

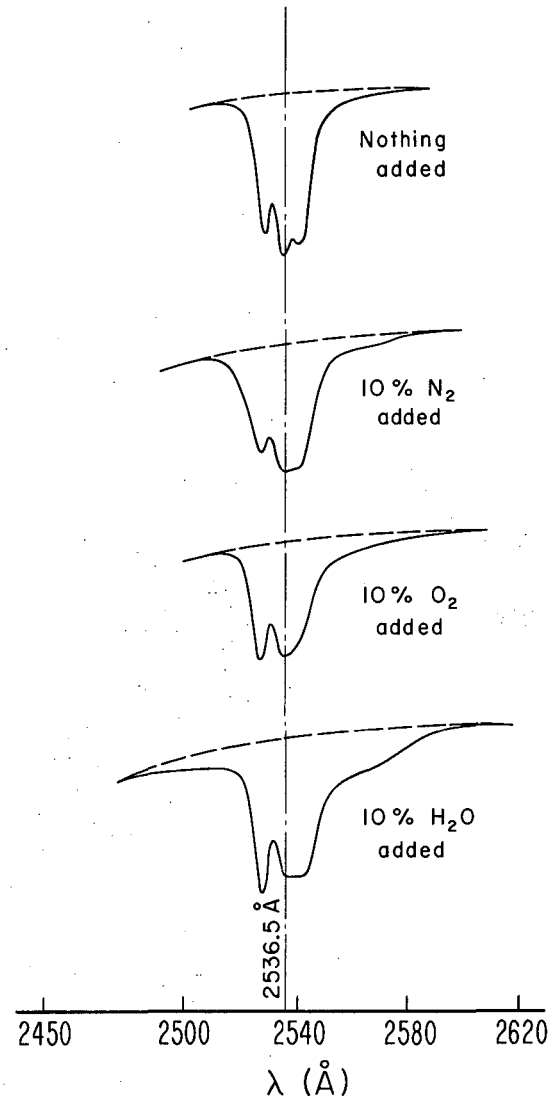
Nothing added
10 % N_2 added
10 % O_2 added
10 % H_2O added
2536.5 Å
2450
2500
2540
2580
2620
λ (Å)
MU-35287

Fig. 4

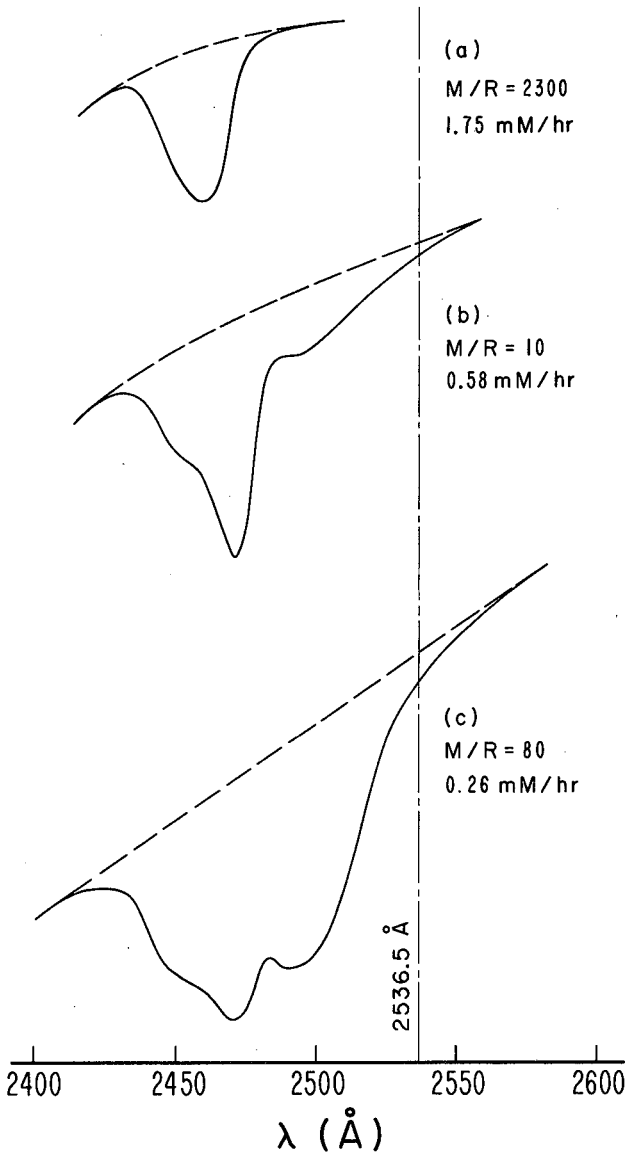
(a)
M/R = 2300
1.75 mM/hr
(b)
M/R = 10
0.58 mM/hr
(c)
M/R = 80
0.26 mM/hr
2536.5 Å
2400
2450
2500
2550
2600
λ (Å)
MU-35288

Fig. 5

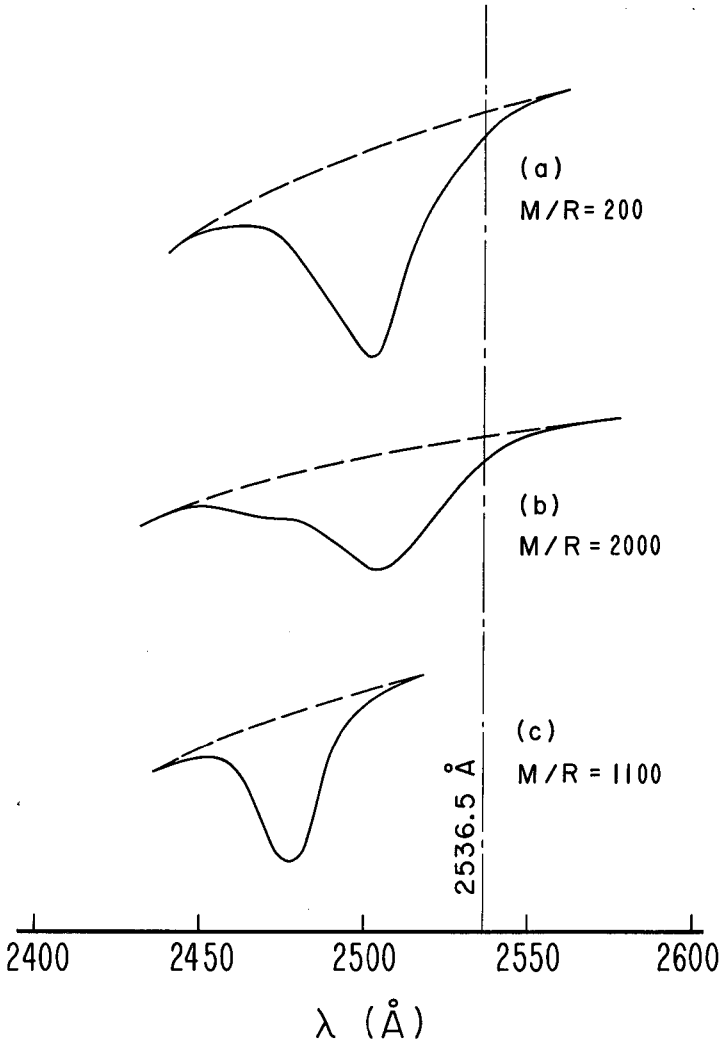
(a)
M/R= 200
(b)
M/R = 2000
(c)
M/R = 1100
2536.5 Å
2400
2450
2500
2550
2600
λ (Å)
MU-35289

Fig. 6

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