

Lawrence Berkeley National Laboratory

Recent Work

Title

THE UV ABSORPTION SPECTRUM OF TRAPPED S₂

Permalink

<https://escholarship.org/uc/item/1px2s574>

Authors

Brewer, L.
Brabson, G.D.
Meyer, B.

Publication Date

1964-09-01

University of California
Ernest O. Lawrence
Radiation Laboratory

THE UV ABSORPTION SPECTRUM OF TRAPPED S_2

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

THE UV ABSORPTION SPECTRUM OF TRAPPED S_2

L. Brewer, G. D. Brabson, and B. Meyer

September 1964

~~Li~~

The UV Absorption Spectrum of Trapped S₂

L. Brewer, G. D. Brabson¹, and B. Meyer²

Inorganic Materials Research Division,
Lawrence Radiation Laboratory
and Department of Chemistry, University of California
Berkeley, California

Abstract

The UV absorption spectrum of trapped S₂ has been studied in N₂, Ar, Kr and Xe matrices at 4° and 20°K. Up to 26 vibrational bands of the v''=0 progression of the $3\Sigma_u^- \leftarrow 3\Sigma_u^-$ system were observed. In each of the matrices, the origin of the transition was shifted by an amount characteristic of the particular matrix; red shifts were observed for Xe, Kr and Ar, while N₂ yielded a blue shift. The vibrational spacing indicated distortion of the potential energy curve under the influence of the matrix field. The absorption bands were slightly shaded towards the blue and had a half width of about 150 cm⁻¹. At low v' doublet structure was observed.

¹ Capt. USAF, Sponsored by the Air Force Institute of Technology

² Present Address: Chemistry Department, University of Washington, Seattle 5, Washington

I. Introduction

Several attempts have been made to trap $S_2^{1,2,3,4}$ but they have been

-
- (1) H. Staudinger and W. Kreis, *Helv. Chim. Acta*, 8, 71 (1925).
 - (2) F. O. Rice and C. Sparrow, *J. Am. Chem. Soc.*, 75, 848 (1953).
 - (3) P. W. Schenk, *Angew. Chem.*, 65, 325 (1953).
 - (4) B. Meyer, *J. Chem. Phys.*, 37, 1577 (1962).

B. Meyer and E. Schumacher, *Helv. Chim. Acta*, 43, 1333, (1960).

hampered for two reasons. First, the composition of sulfur vapor changes as a complex function of temperature and pressure, and the gas phase can contain up to ten different molecules in equilibrium.⁵ Second, hot S_2

-
- (5) J. Berkowitz and J. R. Marquart, *J. Chem. Phys.*, 39, 275 (1963).

molecules, striking a cold target, can react with each other and with their reaction product to give a variety of new sulfur molecules. The trapped vapor, therefore, constitutes, even under the most favorable conditions, a complex mixture.

The objectives of the present work were: to examine the experimental conditions under which S_2 molecules can be isolated in inert gas matrices; to demonstrate the existence of this molecule in these low temperature solids, and to study the appearance of the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition of S_2 in this environment. The matrix spectra were correlated to the well known gas phase bands and compared with the results of analogous observations

for O_2 , for which the corresponding transition (the Schumann-Runge bands) has been studied in Ar and N_2 .^{6,7}

(6) K. Dressler and O. Schnepf, unpublished work.

(7) A. M. Bass and H. P. Broida, J. Mol. Spectroscopy, 12, 221 (1964).

II. Experimental

Three experimental systems were combined for the preparation of the matrix: a gas flow system, a molecular beam furnace, and a cryostat with windows for optical studies. Figure 1 shows the quartz double furnace in which the molecular beams of sulfur were produced. An electrically heated bath of Wood's alloy was used to keep the sample tube at a constant temperature and regulate the sulfur vapor pressure. The equilibrium composition of the sulfur vapor leaving the furnace was regulated by the temperature of the electrically heated horizontal tube between the sulfur reservoir and the orifice. The orifice diameter was varied from 0.05 mm to 1 mm for different furnaces. This made it possible to choose the desired pressure gradient between the furnace and the cryostat for each experiment. A water cooler separated the orifice from the window flange and was shaped so that only a few square millimeters of hot surface were visible to the target. The furnace was connected with a window flange to the metal cryostat. An O-ring seal made it possible for the target to be turned 90° during the course of an experiment in such a way that it either faced the molecular beam or that it was lined up in the optical path of a spectrometer. A simple flow system connected the inert

gas storage bulbs with the cryostat. It consisted of a mercury manometer for measuring the bulb pressure, a needle valve, and a Fischer-Porter type flow meter.

The sulfur used was 99.999% pure, supplied by the American Smelting and Refining Company. Argon, krypton, xenon and nitrogen were high purity Linde or equivalent quality. Most experiments were done with liquid hydrogen as refrigerant, but liquid helium was also used.

Typical values for the sulfur vapor pressure, the orifice temperature, the target temperature, the inert gas flow rate, the S_2 flow rate, the matrix to S_2 ratio (M/R), the total amount of sulfur condensed, and the cryostat temperature and pressure are given in Table I.

To prevent surface effects which could have influenced the active species, the sulfur beam was usually started later and stopped earlier than the inert gas beam. The orifice temperature⁵ was chosen to give a vapor composed of more than 98% S_2 . In most cases a layer of constant S_2 concentration was deposited on the target, but in other experiments the concentration was slowly increased and decreased in order to observe the influence of concentration changes. The preparation time varied between 20 minutes and 10 hours. The maximum flow rate was restricted by the heat exchange through the sample and the target. The mean free path for particles between furnace and the target, estimated from the pressure in the cryostat, was at all times larger than the beam length.

Spectra were photographed with a Jarrell-Ash f/6.3 Czerny-Turner spectrograph in the first order of a 2160 lines per millimeter grating blazed for 3000 Å. The dispersion was 5 Å per millimeter. A 2KW hydrogen discharge, a Xe pressure arc and a tungsten ribbon lamp were used as light

Table I
Experimental Parameters

	Sulfur Vapor Pressure in Furnace (mm Hg)	T orifice (°K)	T target (°K)	Matrix Gas Flow Rate (μmole/min)	S ₂ Flow Rate (μmole/min)	M/R	Total Sulfur Deposited (μgm)	P cryostat (mm Hg)
Typical Experiment	0.005	1000	20	20	0.05	400	100	2×10^{-6}
Minimum and Maximum Values	0.001 8	700 1200	4 76	0* 50	0.01 0.1	0* 3000	10 4000	1×10^{-6} 9×10^{-6}

* In some experiments, no matrix gas was used and the sulfur was allowed to form its own matrix.

sources for different spectral regions. For studies in the UV, a crystal quartz lens and sapphire windows and targets were used. In some experiments, a solution of $\text{NiSO}_4\text{-CoSO}_4$ was placed in front of the cryostat to absorb radiation longer than 3500 Å and to reduce heating of the target. During a standard experiment, cell spectra were taken every twenty minutes, starting with the empty target. For investigation with a Perkin-Elmer model #421 spectrometer, the cryostat was equipped with CsI windows and target. In this way, it was possible to record UV and IR spectra of the same deposit.

III. Results

The results of investigation in the ultraviolet region depended upon the concentration of sulfur in the matrix. For thin deposits with small M/R , an absorption edge at 2400 Å was noted. With continued condensation this edge shifted towards 3100 Å. Deposits containing more than about 500 micrograms sulfur showed a purple color.

Matrices with an S_2 concentration $< 0.5\%$ gave a distinctive band spectrum between 2400 and 3100 Å. Figure 2a shows the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition of S_2 vapor. Figure 2b is a reproduction of a typical spectrum of S_2 in a xenon matrix at 20°K. Both exposures were taken with the same equipment, but for the second exposure a quartz cell of 10 cm length with 0.8 mm Hg sulfur vapor at 1000°K replaced the cryostat.

Table II lists wavenumbers for the band heads in the gas phase⁸

(8) B. Rosen, Constantes Sélectionnées Données Spectroscopiques Concernant les Molécules Diatomiques, Hermann and Company, Paris (1951).

Table IIa
Absorption Spectrum of S₂

v'	Gas Phase ¹ Band Heads (cm ⁻¹)	Matrix ² Absorption Maxima (cm ⁻¹)			
		Xenon	Krypton	Argon	Nitrogen
0	31690 ³	30780	31390	31700	31895
1	32115 ³	31200	840	32100	32335
2	540 ³	635	32285	545	745
3	960	32065	730	945	33145
4	33355	490	33150	33360	560
5	775	905	580	725	955
6	34160	33320	34010	34135	34345
7	560	725	425	520	750
8	955	34135	840	905	35140
9	35340	525	35240	35280	530
10	715	915	640	650	920
11	36100	35305	36030	36020	36300
12	470	685	415	375	675
13	830	36060	805	725	37055
14	37195	435	37185	37075	445
15	550	805	555	420	835
16	895	37165	940	750	38220
17	38230	525	38315	38080	580
18	555	885	670	415	950
19	885	38235	39050	730	
20	39220	580		39045	
21	535	935		345	
22	39850	39285		39675	
23	40140	540		960	
24	445	905		40215	
25	710			520	
26	41010				
27	280				

¹ Reference 8

² All measurements are believed to be accurate to within ± 15 cm⁻¹; additional absorption maxima are listed in Table IIb.

³ Computed from T_e , ω_e and ω_x . These gas phase bands are completely covered by bands from $v'' = e_1, 2$, and 3 and have not yet been observed.

and the absorption maxima in argon, krypton, xenon and nitrogen matrices. Experiments were also made with neon and oxygen matrices, but no discrete absorption was detected. The absorption maxima were obtained from density tracings such as shown in Figure 3; all measurements are believed to be accurate to within $\pm 15 \text{ cm}^{-1}$. The half width of the absorption bands was about 150 cm^{-1} . The bands are weakly but clearly shaded to the violet. In the case of the krypton matrix, the long wavelength bands seemed to be split into doublets; the spacing of these doublets decreased with increasing ν' . In argon and nitrogen, near the origin, additional bands were also found (Table IIb).

During warm-up of the samples the absorption bands became weaker and disappeared into a continuum which overlapped the whole spectral region when the matrix gas evaporated. In thick films, a distinctive color change was observed during the warm-up. The hydrogen lamp emission did not seem to destroy the trapped S_2 , even with long exposures, but a magnesium flash produced immediate aggregation on the target.

Thick films showed an additional broad continuum with a maximum absorption at around 4900 Å. This absorption had been observed earlier⁴ and was found only at high sulfur concentrations. No vibrational structure was observed and it seems likely that this absorption was caused by a molecule containing more than two sulfur atoms.

In some experiments the infrared absorption spectrum was also measured. In very dilute samples (large M/R) the forbidden S_2 vibration⁴ could not be observed. However, with a sulfur concentration of about 0.5% the bands listed in Table III were found. With the exception of the neon and sulfur matrices, the samples used for the IR spectra also gave UV spectra having

Table IIb

Additional Absorption Maxima (cm^{-1})

Krypton	Argon	Nitrogen
31 620	31 825	32 225
32 035	32 220	635
450	645	33 035
845	33 030	435
	375	850
	765	
	34 060	
	185	

Table III

Infrared Absorption of Trapped S₂
in Inert Gas Matrices

Matrix	Frequency (cm ⁻¹)*		
Nitrogen	666		679
Xenon	660		682
Krypton	659	664	685
Argon	660		680
Neon		675	
Sulfur		668	

* All measurements are believed to be accurate to within ± 3 cm⁻¹.

clearly resolved bands. When the matrix was warmed and the matrix gas was pumped off leaving a sulfur matrix, the low frequency band disappeared and the high frequency band shifted to a position at 668 cm^{-1} , common to all experiments. Besides the bands listed in Table III, additional IR bands were observed in nitrogen matrices.

IV. Discussion

All spectra observed in the ultraviolet are here attributed to the ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition of S_2 . This assignment is based upon five observations: (1) The absorption intensity was proportional to the amount of S_2 vapor deposited. (2) The red end of the matrix absorption was in all cases within 950 cm^{-1} of the (0,0) band head of the gas phase absorption at 31690 cm^{-1} . The spectral shift is, therefore, smaller than 3% of the transition energy. (3) The ω'_0 calculated from the matrix spectra was within $\pm 25 \text{ cm}^{-1}$, or 6% of ω'_0 of the gas phase ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition (Table IV). (4) The $\omega'_0 x'_0$ value derived from the matrix spectrum was in all cases within a factor of three of the gas phase value. (5) The matrix bands showed an intensity distribution which corresponded to the Frank-Condon distribution expected from the r_e values of the two states involved.

The nature of the observed absorption in the matrix depended upon the concentration of S_2 . For samples with an M/R smaller than 50 only a continuum extending from 3100 Å to shorter wavelengths was observed; the cut-off at around 3100 Å corresponds to the red end of the $v''=0$ progression. The lack of vibrational structure could be due to absorption saturation⁷ or broadening resulting from the perturbation by nearby sulfur

Table IV
Vibrational Constant of S_2 ($^3\Sigma_u^-$)

Medium	ω'_0 cm^{-1}	ω'_{00} cm^{-1}
gas	431	2.7
Xe	435 ± 3	2.2 ± 0.1
Kr	449 ± 4	2.4 ± 0.2
Ar	426 ± 6	2.9 ± 0.2
N_2	408 ± 4	1.0 ± 0.2

molecules in the matrix. A similar effect has been observed for O_2 in argon.⁶

In comparing gas and matrix spectra one notes that the matrix spectra are much simpler and consist only of a single progression with $v''=0$. The gas phase spectrum is, on the other hand, characterized by several progressions of broad and overlapping bands. The reason for this is that the S_2 molecule is the predominant species in the gas phase only at temperatures where the population of excited vibrational and rotational levels becomes important. At $1000^\circ K$, for example, a third of the molecules is already in the $v''=1$ level and the maximum rotational population is at $J=30$. In the matrix at $20^\circ K$, however, only $v''=0$ is populated, and even if free rotation were assumed, only about 10 rotational levels would be expected to be important, since the maximum population would be at $J=4$.

The observed band width in the matrices is 150 cm^{-1} . The reason for the band width is not yet known, but several contributing factors can be suspected: lattice vibrations, different matrix sites, and the splitting of states in the matrix field. The same factors are also thought to cause the weak violet shading of the bands.

In some matrices doublets are observed for small v' . The two components have, at $v'=0$, comparable intensity. The splitting and intensity of one component seems to decrease with increasing v' , and the weaker component disappears at about $v'=5$. It is unlikely that this splitting can be attributed to the F-level splitting which is only about 12 cm^{-1} in the gas phase.⁹ It is also unlikely that these bands are

(9) R. F. Barrow and J. M. Ketteringham, *Can. J. Phys.*, 41, 419 (1963).

caused by a different transition of S_2 , because there is no state close enough to absorb in an overlapping region unless one makes the doubtful assumption that some molecules are trapped in an excited state, for example the $^1\Delta$, which is expected to lie about 4000 cm^{-1} above the ground state.

From Table IIa it can be seen that the origin of the transition, T_{00} , is shifted. This indicates a change of spacing between ground state and excited state. Such a change in transition energy can be due to a change of the potential energy in both the ground and the excited state. Figure 4 compares the $\Delta G'$ values in the gas and in matrices. One observes that the vibrational frequencies, ω'_0 , and $\omega'_{x'_0}$ are changed in the matrices (see Table IV). This effect indicates a change in the shape of the upper state potential curve. In the case of krypton, the vibrational frequency of the upper state is on the average about 10 cm^{-1} higher than in the gas phase, indicating a considerable "squeezing" of the potential curve. In nitrogen, ω'_0 and $\omega'_{x'_0}$ are significantly smaller; the close approximation to a harmonic oscillator potential results in a change in $\Delta G'$ from a value smaller than the gas value at small v' , to a value larger than the gas value at high v' .

It is planned to examine the fluorescence of S_2 . Such work would make it possible to study the characteristics of the lower state under the influence of matrix fields. The lower state has an r_e value which is about 20% smaller than that of the upper state of the studied transition, and it might be that the same matrix exercises a different influence on the two states; for example, an increase in ω for the state with large r_e , i.e. the upper state, but perhaps a decrease in ω for the state with small r_e , i.e. the ground state.

The shifts in the matrices are comparable with the vibrational frequency of the excited state. This made the vibrational numbering difficult. The proposed numbering of the vibrational levels is based on the assumption that the band with the lowest frequency observed in thick films can be taken as the (0,0) band. However, because of the large change in r_e in this molecule, about 0.3 Å, the bands near the origin have greatly diminished intensities, and it was experimentally difficult to be certain that the (0,0) band had in fact been observed. Using the comparable system in O_2 as a guide¹⁰, one can estimate that

(10) W. R. Jarman, Can. J. Phys., 41, 1926 (1963).

the Franck-Condon factor for the (0,0) band would be considerably less than a half but more than a tenth of that for the (1,0) band. Thus the present work does not exclude the possibility of the existence of additional weak bands. It would have been desirable to ascertain the numbering with isotope experiments, but only sulfur 32 was available.

The IR data indicated that the ground state of S_2 might be split in matrices. The additional bands observed in nitrogen matrices indicate that the S_2 reacts partly with nitrogen. In solid neon the infrared spectrum showed only one band, and the UV absorption was continuous. This indicates that under our conditions the heat dissipation from hot S_2 condensing on solid neon prevented the trapping of isolated S_2 . The band at 668 cm^{-1} , observed in all samples after evaporation of the matrix gas, has already been assigned⁴ to the influence of a 'self matrix' of sulfur on S_2 . S_2 seemed to react with oxygen, and no spectra of S_2 trapped in solid O_2 could be observed.

It is planned to expand simultaneous UV and IR experiments in order to study warm-up processes, and it is hoped that the amount of S_2 deposited in matrices can be increased, so that it becomes possible to observe weak transitions such as ${}^3\Sigma_u^+ \leftarrow {}^3\Sigma_g^-$. The corresponding bands have been observed for O_2 at 36096 cm^{-1} .¹¹ In S_2 the (0,0) band is expected to lie at about

(11) G. Herzberg, Naturwiss., 20, 577 (1932).

23000 cm^{-1} . In the gas phase this region cannot be studied since it is entirely blotted out by the strong ${}^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition.

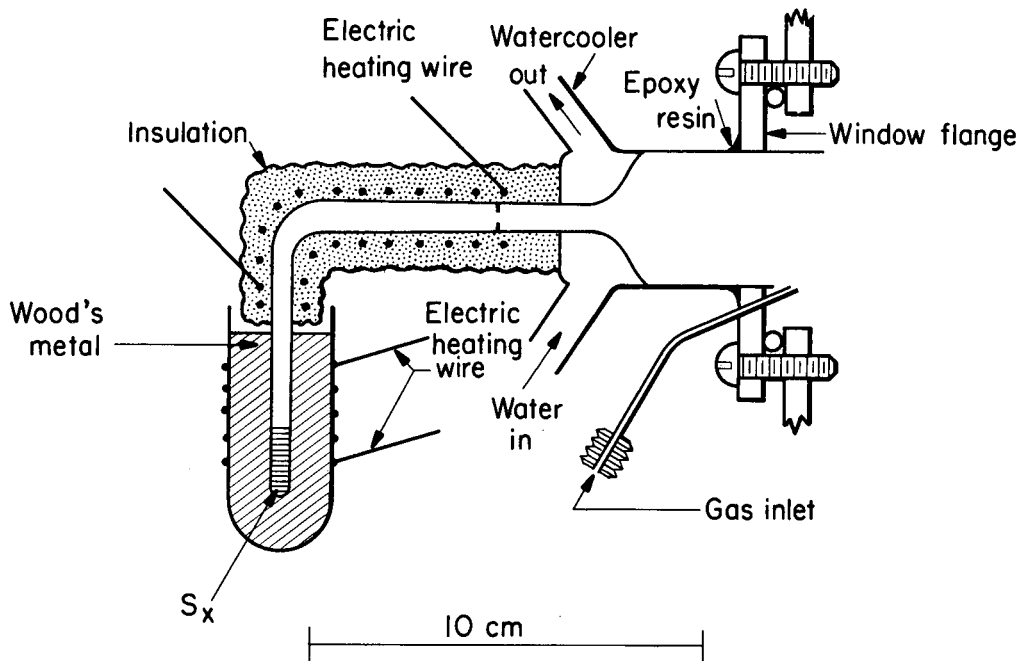
Acknowledgement: The authors wish to thank Dr. K. Dressler for valuable and stimulating discussion.

This work was performed under the auspices of the U. S. Atomic Energy Commission.

Figure Captions

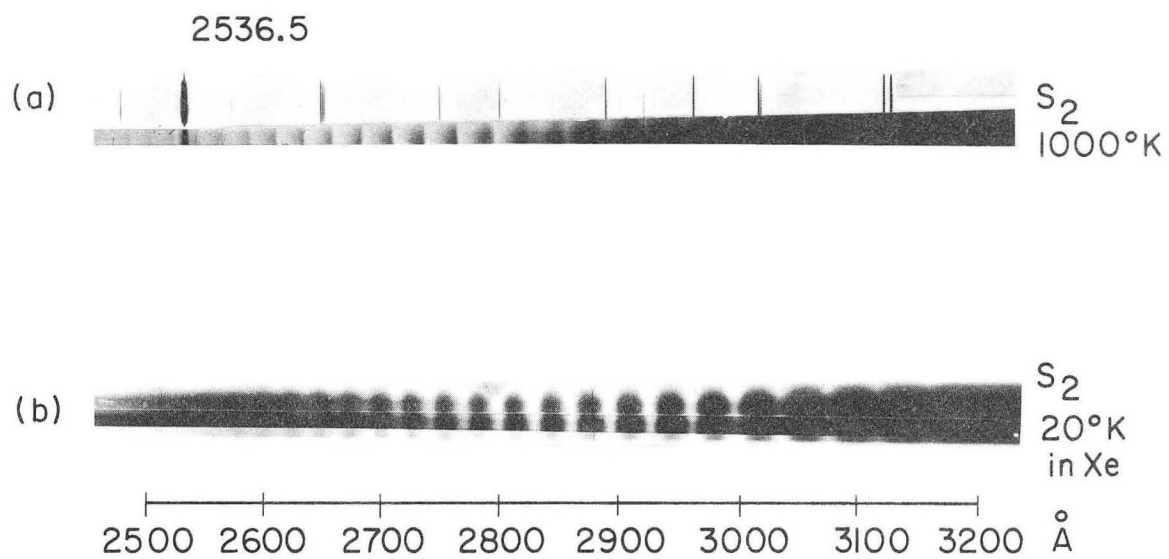
1. Sulfur Double Furnace
2. Absorption Spectrum of S_2 in the Gas Phase (2a) and in Solid Xe (2b)
3. Density Tracing of S_2 in a Xenon Matrix
4. $\Delta G'$ Values for Xe, Kr, Ar, and N_2 Matrices and for the Gas Phase

The lines shown in this figure were obtained by a least squares fit of the data points; the individual points fall in some cases as much as $\pm 20 \text{ cm}^{-1}$ from the lines.



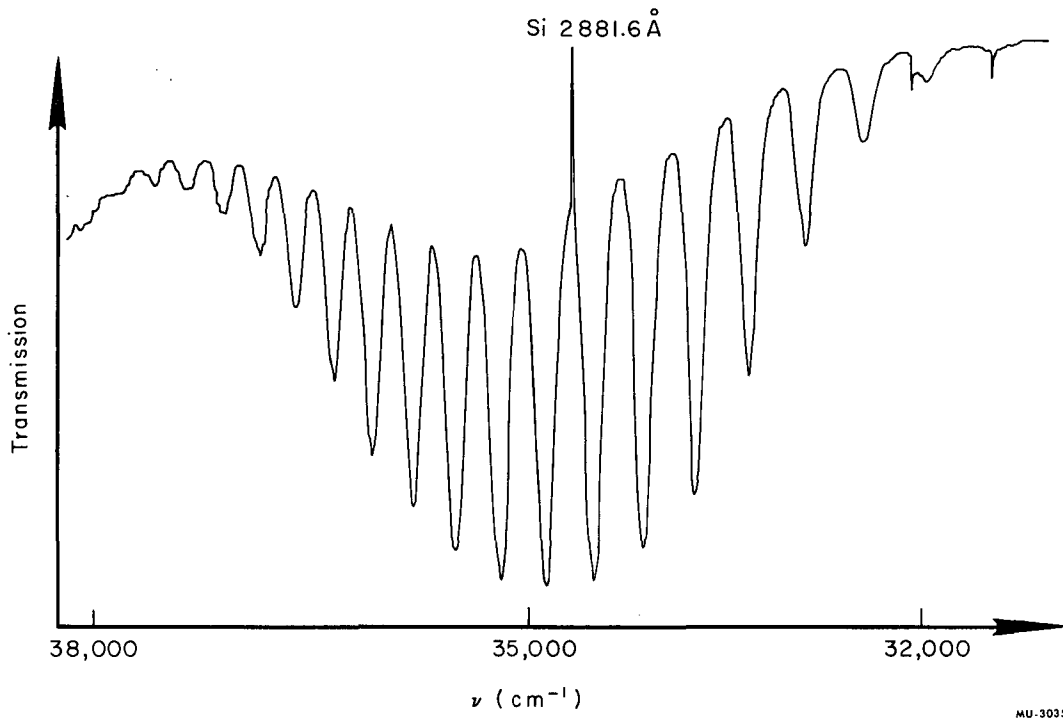
MU-30354

Fig. 1



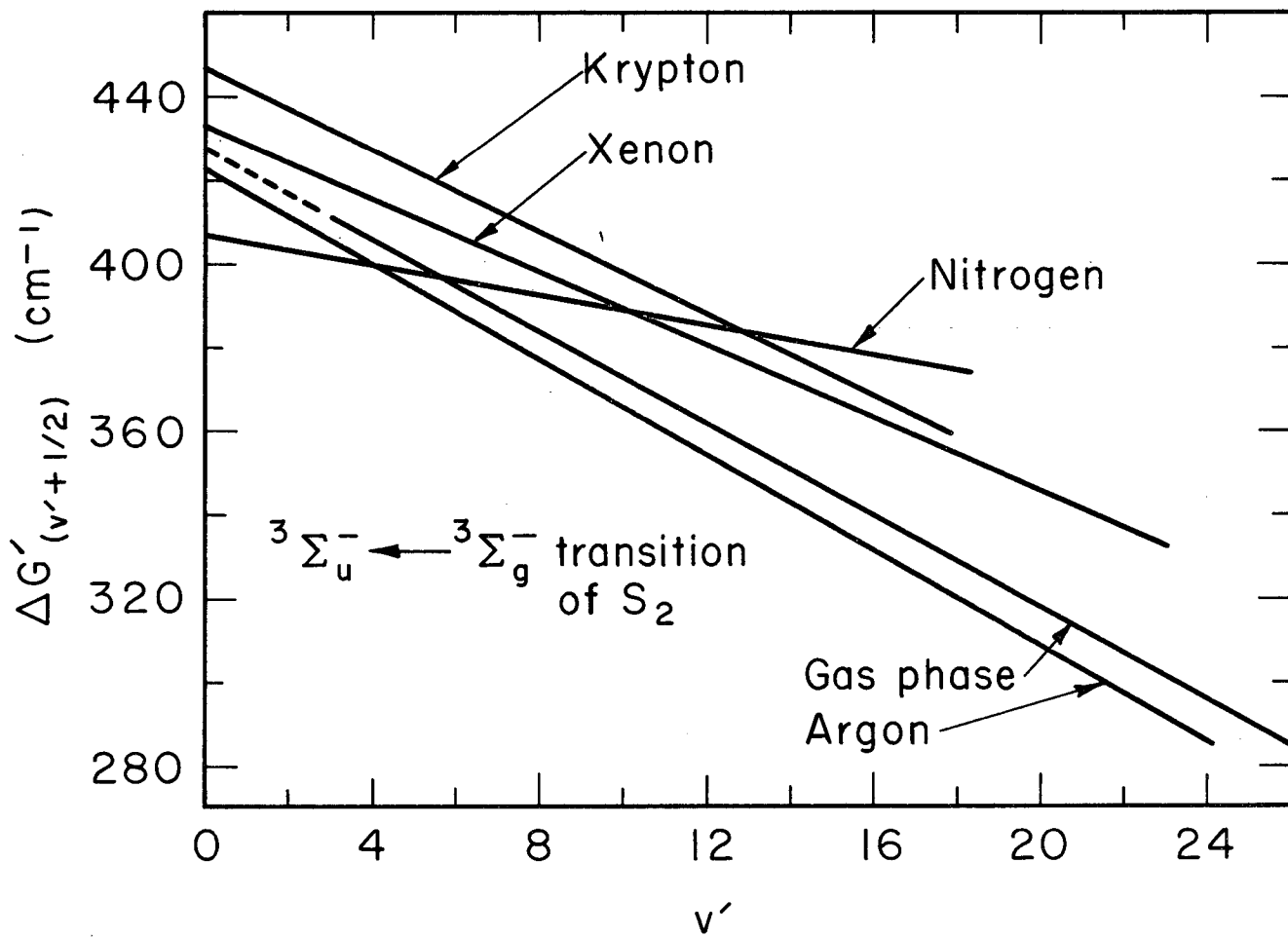
ZN-3940

Fig. 2



MU-30353

Fig. 3



MUB-3887

Fig. 4

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

