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April 1971

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ABSORPTION SPECTRUM OF THE Mg_2 MOLECULE IN SOLID RARE GASES

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ABSTRACT

The Mg_2 molecule has been synthesized in solid rare gas matrices at 20 K. The absorption bands of the Mg_2 molecule found between 3750 Å - 4100 Å are correlated to the $A^1\Sigma \leftarrow X^1\Sigma$ transition between a very weakly bonded ground state and a more stable excited state. Some less well understood features are also reported and tentative explanations are presented.

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I. Introduction:

The present work arose from an attempt to understand the spectral behavior of metal atoms in matrices as a function of metal concentration and the diffusion mechanism of metal atoms in solid rare gases. In these studies, Mg_2 spectral bands were observed in addition to atomic features when Mg was condensed with Kr or Xe.

Diffusion of lithium atoms in solid rare gases at temperatures lower than 50 K has been demonstrated by Andrews (1) and Belyaeva (2). However, for heavier metal atoms, i.e., Mg, Ca, etc., production of dimers from atoms upon warming the matrix is not observed (3). Mg can be cycled reversibly up to 45 K in Kr and up to 65 K in Xe without change of the relative intensities of dimer and monomer. Upon warming to higher temperatures, the rare gas largely vaporizes before appreciable diffusion of the metallic atoms occurs and the absorption disappears.

Estimation of the Mg_2 partial pressure in the Knudsen cell source shows that the concentration of Mg_2 is negligible in the temperature range used. Thus any formation of Mg_2 molecules must take place during the condensation process under conditions of poor thermal contact or of relatively fast deposition to provide a high enough surface temperature and mobility to allow dimerization of Mg atoms before they are frozen into the matrix.

The gas phase Mg_2 spectrum had been reported previously in emission by Hamada (4) and Strukov (5) and in absorption by Sthapitanonda (6), Weniger (7), and Balfour and Douglas (8). Only Balfour and Douglas did the high resolution analysis necessary to establish unambiguously the molecule responsible for the spectrum.

II. Experimental:

The metal cryostat using liquid hydrogen as refrigerant was described in an earlier publication (9). A stainless steel Knudsen cell was constructed for these experiments. It has an orifice with a diameter of 1 mm. The cell was placed in a quartz heater tube which was wrapped with resistance heating wire, and was lined inside with tungsten foil to prevent stray atoms from reaching the quartz.

A magnetically operated shutter is used to interrupt the atomic beam from reaching the target while the furnace is outgassing. The furnace temperature was between 330 to 360 C as measured by a Chromel Alumel thermocouple (type K).

The matrix gas flow was controlled by an independent inlet system and the quantity of condensed gas was estimated from the geometry of the system and the calibrated leakage rate. During deposition the cryostat pressure was always less than 6×10^{-6} torr. The estimated value of M/R (moles of matrix/moles of radical) was typically of the order of 100 or below. Rate of metal deposited is approximately 6×10^{-6} mole/sec. High purity (> 99.99%) rare gases are used without further purification. The sublimed magnesium metal was provided by Dow Chemical Co. with a purity of 99.994%.

The spectra are photographed with a 0.75 meter Jarrell-Ash plane grating spectrograph, model 75-000. The ultraviolet continuum source is provided by a 150 watt xenon-mercury arc lamp operating at 8 amp. A high intensity tungsten lamp is used as a light source for visible region. Spectral images are photographed on Kodak 103-a-O spectroscopic plates.

III. Observations and Interpretations:

Absorption spectra of magnesium have been observed in both Kr and Xe matrices. They are shown in Figs. 1, 2, and 3. The bands are listed in Tables I, II, and III. The spectral region from 7000 Å to 2100 Å was studied. No observable bands are seen above 4100 Å.

(A) 3700-4100 Å region

In this region there is a discrete band system. There is an approximately constant matrix shift of 700 cm^{-1} from Kr to Xe matrix. The vibrational spacing is very close to the gaseous vibrational spacing of A $^1\Sigma_u^+$ Mg_2 reported by Balfour and Douglas (8). The bands in both Kr and Xe are shifted to the red compared to the gaseous A $^1\Sigma^+ \leftarrow$ X $^1\Sigma^+$ spectrum. A gas phase potential curve for the A $^1\Sigma^+$ state of Mg_2 is shown in Fig. 4 and the observed levels in Kr and Xe matrices are also included for comparison. The assignment of vibrational levels for the matrix spectra is not to be considered as exact because no isotopic substitution experiments were done. As will be discussed more fully in Section IV, the ground state of Mg_2 correlates with ground state atoms and the excited state correlated with $Mg(^1S) + Mg(^1P)$.

(B) 3540-3700 Å region

In the Xe matrix there is a broad absorption band in this region. This band degrades to the blue with a sharp cutoff at the red edge, and it remains as one broad diffuse band as the temperature of the matrix is increased.

In Kr there are two bands in this region. The short wavelength band has the same appearance as the band in Xe. The long wavelength band resolves into a doublet as the temperature is increased, with the long wavelength component shifting to the red while the other component diminishes. The long wavelength component is at the wavelength that would be expected for the $^3D \leftarrow {}^3P_3$ transition of Mg. Such an interpretation would require optical pumping of $^1P \leftarrow {}^1S$ and radiationless decay to the ^3P state. If this interpretation were correct, the short wavelength component of the doublet would be ascribed to the same transition for atoms in an unstable matrix site as the short wavelength component disappears upon warming of the matrix. A similar transition is observed in xenon but the matrix shift merges it into the broad adsorption band region. The broad absorption band in both Kr and Xe may be due to a polymer or to a transition between two relatively unstable molecular electronic states of Mg_2.

(C) 3100-3250 Å region

In this region only a broad band appears in both Kr and Xe matrices. This band appears together with the 2700-4100 Å discrete band system, but it may be due to polymeric magnesium.

(D) 2960-3000 Å

An absorption band appears in the Xe matrix only when the magnesium concentration is very high and very often it is overlapped by the broad absorption of the Mg $^1P \leftarrow {}^1S$ resonance transition, which is shifted to

the red in Xe compared to the gas. In Kr the band is not overlapped by the Mg resonance absorption, which is shifted to the blue compared to the gas. Thus the absorption band appears very distinctly. This band is very much like an atomic transition.

(E) 2800-2960 Å

The magnesium resonance absorption appears in this region. If the magnsium concentration is very low and the rate of deposition is slow, a triplet feature is observed in this region. This absorption is assigned to the $^1P \leftarrow {}^1S$ transition of atomic magnesium. It has been reported previously by Schnepp (10) and Wang (3). If the magnesium atomic concentration is higher than 1 atomic percent, this band becomes a very broad band without any discrete structure and it remains a broad band when the temperature of the matrix increases. If the magnesium concentration is very low and the rate of deposition is fast, a very broad band appears in this region, but upon annealing the band resolves into triplet features.

(F) 2550-2780 Å

In this region two broad absorptions appear in both matrices; they appear quite symmetrical. The long wavelength one appears in dilute matrices only with fast deposition rates and disappears as the matrix is annealed. This absorption may well be due to some multiple site effect of the resonance transition of atomic magnesium. The short wavelength band appears only at high magnesium concentrations. This

may be tentatively correlated to the $^1\Pi \leftarrow X^1\Sigma$ molecular transition observed in the gas phase by Balfour and Douglas.

IV. Discussion:

The results of the gaseous spectra suggest that the ground electronic state of van der Waals molecules may be unstable or have a very shallow potential minimum. For these molecules, one finds very low values for the dissociation energies and large values for r_e, the internuclear distance.

The potential energy diagrams of A $^1\Sigma_u^+$ and X $^1\Sigma_g^+$ states of gaseous Mg_2 are given by Balfour and Douglas (8). They have shown that the vibrational levels of the upper state of the 3500 Å system of Mg_2 converge to $Mg(^1S) + Mg(^1P)$, thus correlating the A state with the $^1\Sigma_u^+$ state derived from this limit. A comparison of the observed absorption bands in both Kr and Xe matrices with the gaseous observed and calculated values is shown in Fig. 4. The comparison is tentative as isotopic substitution or fluorescent experiments would be required to fix the vibrational numbering unambiguously. This absorption band system is the most distinctive of the observed band systems. There are at least nine bands in the system, which indicates that the upper state is relatively stable. The vibrational levels of the upper state converge to the energy of $Mg(^1S) + Mg(^1P)$ and it seems reasonable to assign the observed upper state to the $^1\Sigma_u^+$ state of Mg_2. The vibrational spacings of Mg_2 in the matrices is almost the same as in the gas phase, but the transition is shifted to the red by at least 900 and 1500 cm^{-1} in Kr and Xe, respectively.

The observed relative intensities of the bands of A $^1\Sigma_u^+ \leftarrow$ X $^1\Sigma_g^+$ in matrices have maxima at $v' = v_o' + 5$, where v_o' is the lowest vibrational state of the observed band. From the Franck-Condon principle, one would conclude that the difference between internuclear distances of the upper and lower states is relatively large. For the gaseous A $^1\Sigma_u^+$ state of Mg_2, r_e = 3.082 Å, while r_e = 3.889 Å for the $X^1\Sigma_g^+$ state. The internuclear distance of the more tightly bound A state would not be expected to change much in the matrix. Comparison of the gaseous and matrix spectra would indicate that the ground state internuclear distance has been compressed below the 3.889 Å of the gaseous molecule but it is still larger than 3.082 Å.

The dissociation energies of the two states are related by the following equation.

$$D_0^o\ (X\ ^1\Sigma_g^+) = \nu_{00} + D_0^o\ (A\ ^1\Sigma_u^+) - E(^1P \leftarrow {}^1S)$$

where ν_{00} is the energy between the v" = 0 and v' = 0 levels, $E(^1P \leftarrow {}^1S)$ is the energy of the resonance transition of Mg. If we use the observed $^1P \leftarrow {}^1S$ transition of Mg in the matrices as the limit for the dissociation of the A state of Mg_2, then the A $^1\Sigma_u^+$ state in the matrix would have a dissociation energy of approximately 10 100 + $D_0^o(X\ ^1\Sigma_g^+)$ in Kr and 9570 + $D_0^o(X\ ^1\Sigma_g^+)$ in Xe as compared to 9311 cm^{-1} for the gaseous molecule. The D_0^o of the ground state is probably increased upon being trapped in a matrix, but if we use the gaseous value of $D_0^o(X\ ^1\Sigma_g^+)$ = 399 cm^{-1}, then for $D_0^o(A\ ^1\Sigma_u^+)$, we calculate 10 500 cm^{-1} in Kr and 9970 cm^{-1} in Xe as lower limits. Thus the A state of Mg_2 is stabilized by more than 1200 and 660 cm^{-1} in Kr and Xe, respectively.

V. Conclusion:

This work can be only regarded as a small effort toward the understanding of dimerization of metal atomis in matrices. It does demonstrate that one can synthesize very unstable molecules like van der Waals molecules and accumulate them in an inert environment relatively free from interaction for a long period of time. While we are able to identify some of the absorption features of the diatomic magnesium molecule, we have not been able to segregate and identify the higher polymers, i.e., Mg_3, Mg_4, etc. This work suggests that great care must be taken in interpreting the continuous absorption bands as due to dimeric species because they may be polymers. During the brief period of mobility on the matrix surface before being covered and frozen into the matrix, it is possible to produce a variety of polymers unless concentrations and deposition rates are kept low.

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

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TABLE I. Absorption Bands of A $^1\Sigma \leftarrow$ X $^1\Sigma$ of Mg_2 in Kr Matrix at 20 K

λ, Å	ν, cm^{-1}	$\Delta G'_{v+\frac{1}{2}}$, cm^{-1}
3963	25233	
		199
3932	25432	
		196
3902	25628	
		192
3873	25820	
		188
3845	26008	
		184
3818	26192	
		193
3790	26385	
		140
3770	26525	
		213
3740	26738	

TABLE II. Absorption Bands of A $^1\Sigma \leftarrow X\ ^1\Sigma$ of Mg_2 in Xe Matrix at 20 K

λ, Å	ν, cm^{-1}	$\Delta G'_{v+\frac{1}{2}}$, cm^{-1}
4078	24522	
		188
4047	24710	
		197
4015	24907	
		181
3986	25088	
		171
3959	25259	
		154
3935	25413	
		169
3909	25582	
		165
3884	25747	
		187
3856	25934	

TABLE III. Other Bands of Magnesium in Rare Gas Matrices at 20 K

Band	Kr		Xe	
	λ, Å	ν, cm^{-1}	λ, Å	ν, cm^{-1}
B	3590	27860		
	3575	27970		
	3544	28220	3691	27090
C	3115	32110	3243	30836
D	2964	33740	2992	33420
E	2852	35060	2952	33870
	2830	35330	2934	34090
	2816	35510	2915	34300
F	2646	37800	2730	36630
	2558	39090	2619	38180

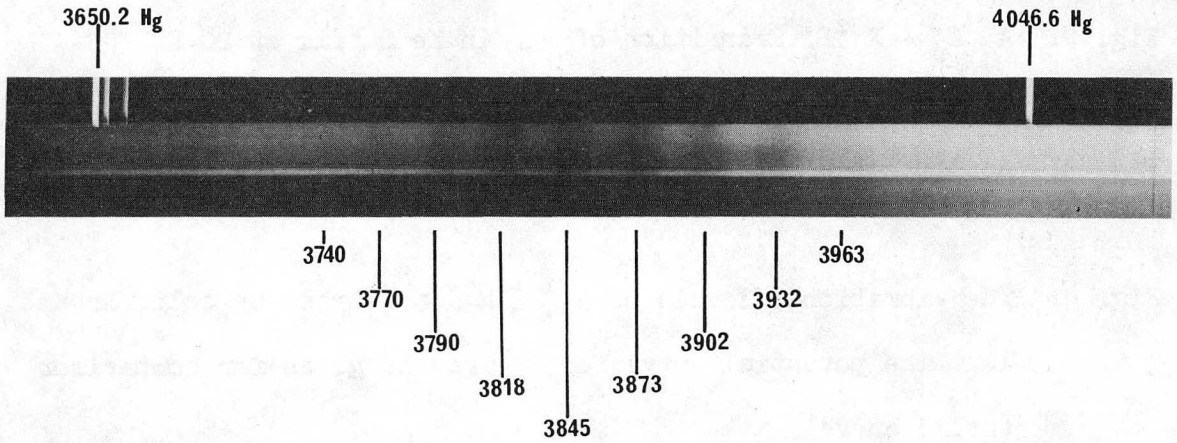
Figure Captions

Fig. 1. A $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ Transition of Mg_2 in Kr matrix at 20 K.

Fig. 2. A $^1\Sigma_u^+ \leftarrow X\ ^1\Sigma_g^+$ Transition of Mg_2 in Xe matrix at 20 K.

Fig. 3. Absorption spectrum of Mg_2 in Xe matrix at 20 K.

Fig. 4. The vibrational levels of A $^1\Sigma_u^+$ Mg_2 perturbed by solid Kr and Xe. The potential curve for Mg_2 gas is given for comparison (solid curve).



WAVELENGTH IN Å

XBB709-4041

Fig. 1.

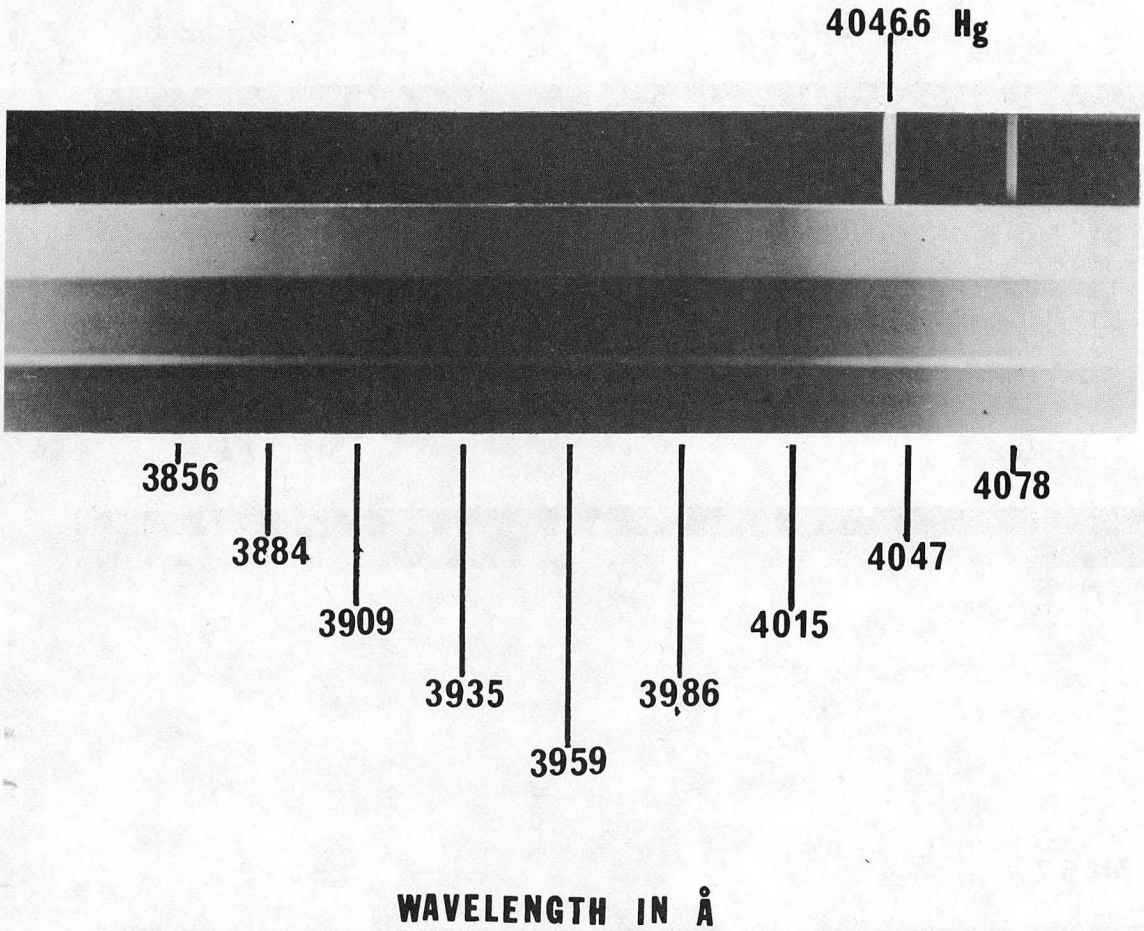


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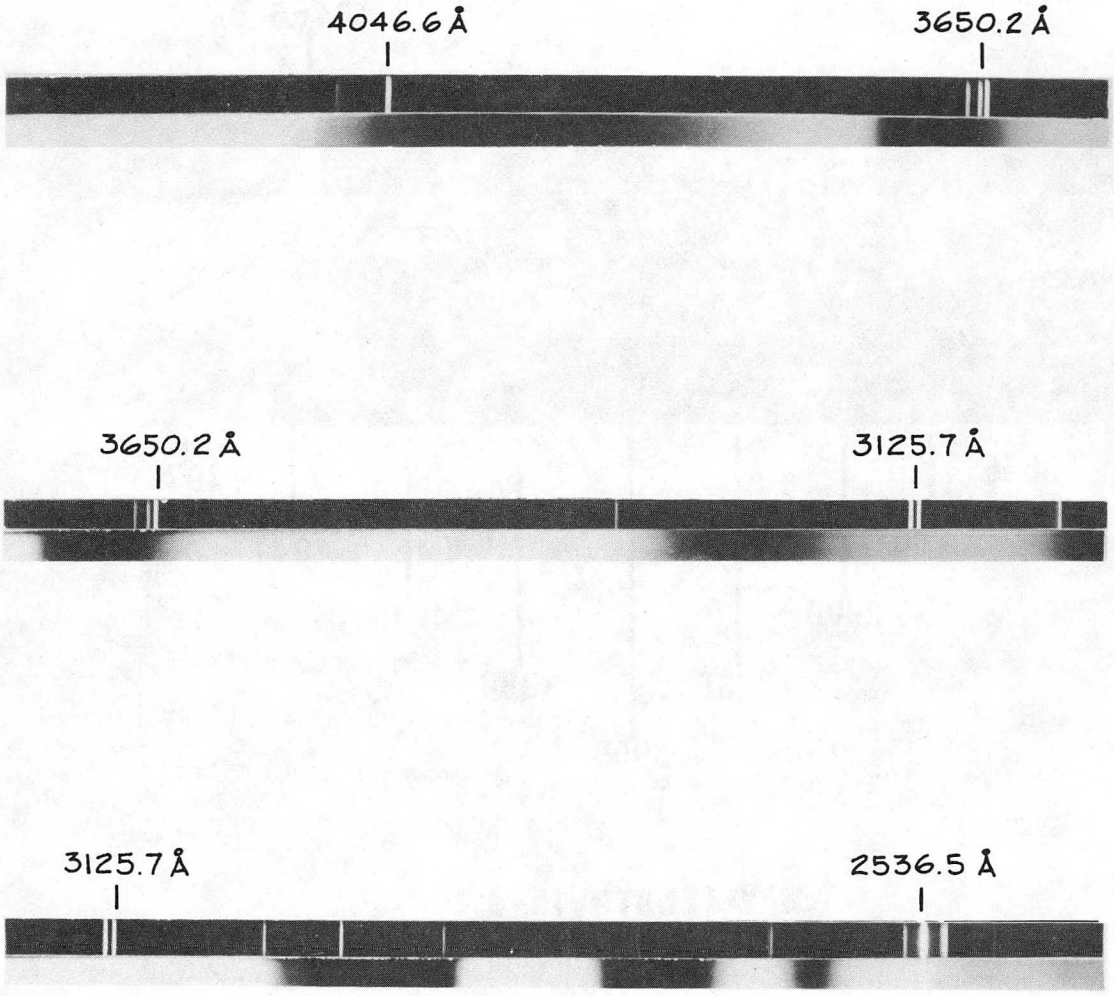
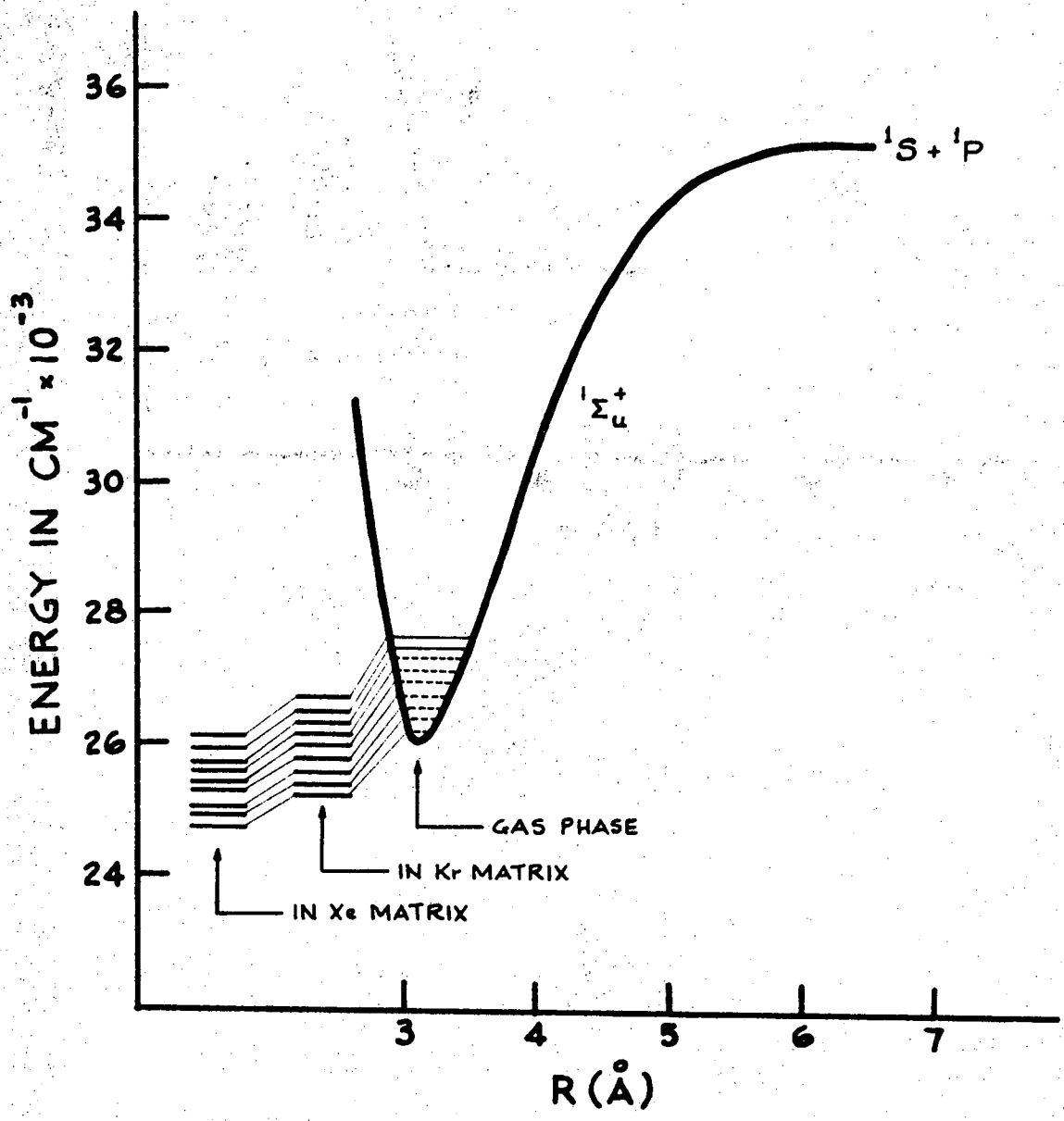
Fig. 2.



XBB713-992

Fig. 3.



XBL713-6605

Fig. 4.

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