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POTENTIAL ENERGY CURVES FOR DIATOMIC ZINC AND CADMIUM

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Bender, C.F.

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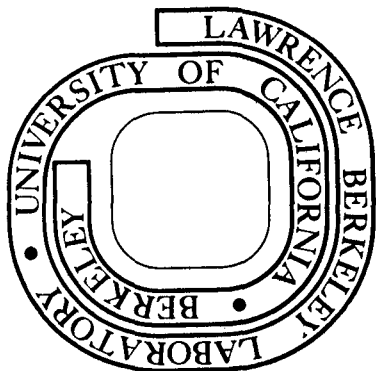
Charles F. Bender, T. N. Rescigno,
Henry F. Schaefer III and A. E. Ore1

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Potential Energy Curves For
Diatomic Zinc and Cadmium

Charles F. Bender* and T. N. Rescigno

Theoretical Atomic and Molecular Physics Group
Lawrence Livermore Laboratory
University of California
Livermore, California 94550

and

Henry F. Schaefer III** and A. E. Ore1**

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

* M. H. Fellow.

** Consultant to Lawrence Livermore Laboratory.

Abstract

Molecular electronic structure theory has been applied to the low-lying electronic states of Zn_2 and Cd_2 . Gaussian basis sets of size $Zn(13s\ 9p\ 5d)$ and $Cd(15s\ 11p\ 7d)$ have been optimized in atomic calculations on the ground 1S and excited 3P electronic states. The general contraction scheme of Raffanetti has been used to reduce these primitive gaussian bases to size $Zn(5s\ 4p\ 1d)$ and $Cd(6s\ 5p\ 2d)$ without any degradation in the atomic SCF energies. Following $X\ ^1\Sigma_g^+$ ground state SCF calculations, full configuration interaction was performed for the four valence electrons. The resulting potential energy curves for Zn_2 and Cd_2 are, with some notable exceptions, qualitatively similar. In the case of Cd_2 , we have obtained potential curves which include spin-orbit coupling and have carried out a detailed analysis of the fluorescence intensity from the first $1_u\ (^3\Sigma_u^+)$ excited state.

Introduction

In recent years there has been considerable interest, both theoretical^{1,2} and experimental,³⁻⁶ in the spectroscopy of the series of molecules Zn_2 , Cd_2 , and Hg_2 . The origin of these studies is the fact that such Group II molecules have been considered prime candidates as high power visible or ultraviolet lasers.⁷ This likelihood in turn arises from the fact that Zn_2 , Cd_2 , and Hg_2 have qualitatively repulsive (except for van der Waals and other classical attractions) ground state potential curves, but a variety of significantly bound, electronically excited potential curves. As in the case of the noble gas halides,⁸⁻¹⁰ this possibility of bound-free transitions is of high interest in gas-laser development.

Two recent theoretical studies^{1,2} have been particularly designed to predict the relativistic potential energy curves of the mercury dimer. In the first Hay, Dunning, and Raffenetti calculated ab initio potential energy curves for Zn_2 and then extrapolated these results to Hg_2 using experimental spin-orbit information from the Hg atom. The second study, that of Mies, Stevens, and Krauss chose the Mg_2 system for the actual ab initio calculations. Then they similarly adjusted the potential curves to yield the exact asymptotic energies for $Hg + Hg$, again using atomic spectroscopic data for the Hg atom to account for relativistic effects.

Both the Hay-Dunning-Raffenetti and Mies-Stevens-Krauss approaches seem to us to be quite reasonable alternatives to the presently impossible¹¹ task of carrying out fully relativistic ab initio studies on Hg_2 itself. Nevertheless, it is not unreasonable to investigate some of the assumptions made in their work. In the present paper, we examine the question of just how

closely related are the potential curves for Zn_2 and Cd_2 . Considerable care has been paid to designing ab initio theoretical procedures which are strictly analogous for the two systems. Thus it is hoped to gain insight into the changes which occur in stepping down one row in the periodic table. Finally, it should be noted that Cd_2 is of considerable interest in itself^{4,12} and a much more plausible candidate for laser action than either Zn_2 or Mg_2 . The fluorescence characteristics of Cd_2 will be considered in a later section of this paper.

Theoretical Approach

As in any electronic structure investigation, our first problem was to identify an appropriate basis set. In their work on Zn_2 , Hay, Dunning, and Raffanetti¹ adopted the (12s 6p 4d) basis set of Roos, Veillard, and Vinot.¹³ However, we preferred a somewhat larger set, comparable to Huzinaga's popular (9s 5p) set¹⁴ for first row atoms. Therefore, it was decided to optimize a new Zn(13s 9p 5d) primitive gaussian basis set. This was accomplished using the ATOM-SCF program of Roos, Salez, Veillard, and Clementi.¹⁵

Our Zn basis set is given in Table I and yields a Zn 1S ground state SCF energy of -1777.68250 hartrees. This result is notably lower than the Roos-Veillard-Vinot energy of -1777.2409 hartrees, but also above the Hartree-Fock limit,¹⁶ -1777.847 hartrees. Actually, only the s, d, and first seven p basis functions in Table I were optimized for the 1S ground state. The outermost two p functions were specifically determined for the $1s^2 2s^2 2p^6 3s^2 3p^6 4s 4p^3 P$ state, as suggested by Hay, Dunning, and Raffanetti.¹ The 3P SCF energy obtained with the basis of Table I is

-1777.58368 hartrees. The corresponding $^1S-^3P$ SCF energy separation is $21,690 \text{ cm}^{-1}$, considerably lower than the experimental value¹⁷ $32,310 \text{ cm}^{-1}$. This is an obvious consequence¹⁸ of the fact that there is more correlation energy associated with the closed-shell singlet ground state than with the 3P state.

The same general approach was followed in optimizing a (15s 11p 7d) primitive gaussian basis set for the cadmium atom. Table II gives the resulting basis, which yields a 1S SCF energy of -5464.83608 hartrees, which may be compared with the Hartree-Fock limit,¹⁶ -5465.142 hartrees. The same basis yields a 3P Cd SCF energy of -5464.75765 hartrees and a $^1S-^3P$ separation of $17,210 \text{ cm}^{-1}$, well below the experimental result, $30,110 \text{ cm}^{-1}$.

In this research we were fortunate to be able to use the general contraction scheme of Raffanetti.¹⁹ The power of this approach is that one can severely contract a large primitive gaussian basis and yet reproduce the totally uncontracted ground state atomic SCF energy. In the present case the inner shell orbitals were fully contracted and a double zeta representation of the valence orbitals was chosen. Thus the full basis sets may be labeled Zn(13s 9p 5d/5s 4p 1d) and Cd(15s 11p 7d/6s 5p 2d).

With these relatively small (given the numbers of electrons) contracted gaussian basis sets, it is possible to carry out rather complete configuration interaction (CI) studies. Here we report full CI calculations on the outer four (valence) electrons of Zn_2 and Cd_2 . Full valence CI studies of this sort are fairly insensitive to the set of molecular orbitals employed, so the $^1\Sigma_g^+$ ground state MO's were used as a convenient basis. The actual CI procedures used the D_{2h} subgroup of the full $D_{\infty h}$ point group. For the

$^1\Sigma_g^+$ states, this involved a total of 1568 $^1A_{1g}$ configurations in the full four electron CI.

The actual total energies obtained are available from the authors but due to space limitations are not included here. For Zn_2 the internuclear distances examined included $R(Zn-Zn) = 4.0, 4.5, 4.75, 5.0, 5.25, 5.5, 5.75, 6.0, 6.25, 6.5, 7.0, 8.0, 10.0, 12.0, 15.0,$ and 40.0 bohrs. For Cd_2 , the points making up the potential curves were $R(Cd-Cd) = 4.0, 5.0, 5.25, 5.5, 5.75, 6.0, 6.25, 6.5, 7.0, 7.5, 8.0, 9.0, 10.0, 12.0, 15.0,$ and 40.0 bohrs.

Results and Discussion

A. Asymptotic Limits

A reasonable first question to ask is how well the present CI methods reproduce the known atomic excitation energies of Zn and Cd. In Table III our theoretical results are compared with experiment. There we see that CI markedly reduces the SCF errors in the theoretical values of $\Delta E(^1S-^3P)$. The SCF, CI, and experimental singlet-triplet separations for zinc are 21,690, 28,170, and 32,310 cm^{-1} . Unfortunately, a sizeable error remains even in the best theoretical treatment.

Hay, Dunning, and Raffenetti¹ note the same problem, and shift their computed potential curves to reflect the experimental asymptotes. While we have followed this procedure in obtaining spin-orbit curves for Cd_2 , the nonrelativistic curves for Zn_2 and Cd_2 reflect the computed unshifted asymptotes. The major effect of an adjustment of the asymptotes is to raise those potential curves dissociating to the $^1S + ^3P$ limit relative to those connecting to $^1S + ^1S$ and to $^1S + ^1P$. Interested readers may obtain the numerical curves from the authors.

B. Potential Energy Curves

The predicted, unshifted potential energy curves for Zn_2 and Cd_2 are seen in Figures 1 and 2, respectively. The overall result of comparing the two figures is the conclusion that the electronic structures of Zn_2 and Cd_2 are qualitatively similar. However, closer inspection shows some differences.

First, the energetic order of the $1\Sigma_u^+$ and $1\Pi_u$ states is reversed between Zn_2 and Cd_2 . However it must be conceded that these two electronic states lie very close to each other for both Zn_2 and Cd_2 , and this is the primary conclusion one should draw concerning their relative positions. A second difference is that for Cd_2 , Figure 2 shows that the repulsive $3\Sigma_g^+$ curve crosses the bound $1\Sigma_u^+$ and $1\Pi_u$ curves at the same value of $r(Zn-Zn)$, the bond distance. That is to say, there is a "triple intersection" of the three potential energy curves. Realistically, however, the fact that the asymptotic limit $Cd(1S) + Cd(3P)$ is predicted to be lower than known experimentally means that the repulsive $3\Sigma_g^+$ curve actually crosses the $1\Sigma_u^+$ and $1\Pi_u$ curves at larger internuclear separations.

A particularly prominent feature of the Zn_2 curves is the maximum in the $1\Pi_u$ potential curve. This maximum was first predicted by Hay, Dunning, and Raffanetti,¹ who predicted a barrier of 0.19 eV. Here we find the $1\Pi_u$ maximum to occur at $\sim 4.2 \text{ \AA}$ with the same barrier height, 0.19 eV. For Cd_2 the $1\Pi_u$ bump occurs near $r = 5 \text{ \AA}$ and its height is notably less, 0.12 eV.

A final qualitative observation is related to the statement by Mies, Stevens, and Krauss (MSK)² that their Mg_2 potential energy curves might be closer to the Hg_2 curves being modeled than are the Zn_2 curves of Hay, Dunning, and Raffanetti (HDR). MSK support this statement by noting that the Mg atom has a greater spatial extent than does Zn and in this sense is a better model for Hg. While we have noted above the qualitative agreement

between our (and those of HDR) Zn_2 and Cd_2 potential curves, it is also true that the MSK curves for Mg_2 are qualitatively similar to our Cd_2 curves. Some qualitative differences include the fact that the Mg_2 potential curves dissociating to ($^1S + ^1P$) atoms are somewhat more spread out than the comparable curves for Cd_2 , and the Mg_2 $^1\Pi_u$ maximum occurs at a smaller internuclear separation than for Cd_2 (and presumably Hg_2).

C. Spectroscopic Constants

The results depicted in Figures 1 and 2 are given quantitative form in Table IV, which gives predicted spectroscopic constants for Zn_2 and Cd_2 . As noted above the only shift in energetic ordering of states is the $^1\Pi_u, ^1\Sigma_u^+$ pair. For Zn_2 the $^1\Sigma_u^+$ state lies 0.08 eV lower, while for Cd_2 the $^1\Pi_u$ state is lower by 0.05 eV.

In addition to the ab initio electronic excitation energies T_e , this quantity has been semi-empirically predicted by correcting the asymptotic $Zn + Zn$ and $Cd + Cd$ dissociation limits to concur with experiment.¹⁷ These results are labeled "Adjusted T_e " in Table IV. There are no startling differences between the Zn_2 and Cd_2 excitation energies T_e . The $^3\Pi_g$ and $^3\Sigma_u^+$ T_e values are comparable, while those for the four bound states dissociating to $M(^1S) + M(^1P)$ are notably less for Cd_2 than for Zn_2 . Although this result is in part anticipated from the lower atomic excitation energy for 1P Cd (than for 1P Zn), Table IV notes that the $2^1\Sigma_g^+$ dissociation energy is 0.17 eV greater for Cd_2 than for Zn_2 .

As expected the Cd_2 bond distances are longer than those for the comparable states of Zn_2 , and those differences all fall in the rather narrow range $0.33 \overset{\circ}{\text{A}}$ to $0.37 \overset{\circ}{\text{A}}$. Except for the $^1\Sigma_u^+$ and $2^1\Sigma_g^+$ states,

our predicted values of r_e (Zn-Zn) agree with those of HDR to within 0.01 or 0.02 Å. For the $2^1\Sigma_g^+$ state, the HDR separation of 3.07 Å is still only 0.11 Å than that of the present work. Considering how shallow this potential well is, such a discrepancy is not surprising.

Intuitively one might expect a uniform relationship between the Zn_2 and Cd_2 dissociation energies D_e , as was found for the bond distances. However, we predict the lower three bound states of Cd_2 to have smaller dissociation energies than those of Zn_2 , while the reverse is true for the upper three states. Vibrational frequencies were predicted for $^{64}Zn_2$ (nuclear mass = 63.9291) and $^{114}Cd_2$ (nuclear mass = 113.0936). The ω_e values are roughly correlated with the predicted dissociation energies, but there are notable deviations. Most obvious is the fact that the Cd_2 $^1\Pi_g$ D_e value is more than twice as large as that for the $^1\Pi_u$ state, while the vibrational frequencies are in the ratio 137:119.

D. Cd_2 Spin-Orbit Curves

Using the experimentally known positions of the 1P_1 and $^3P_{J=0,1,2}$ states of atomic Cd, we have derived a set of potential curves for Cd_2 which reflect the atomic spin-orbit splittings and dissociate to the correct asymptotic limits. The spin-orbit coupling is based on the approximate treatments of Cohen and Schneider²⁰ and Hay, Dunning and Raffenetti.¹ In this scheme, one uses the atomic spin-orbit parameters to determine the matrix elements of the spin-orbit Hamiltonian that couple the molecular states at infinite separation. On the assumption that these matrix elements are independent of R , a set of spin-orbit curves is obtained by diagonalizing the spin-orbit matrix in the basis of the computed electronic energies at the various calculated R -values. The details of this treatment can be found in the paper by Hay, Dunning and Raffenetti.¹

The atomic spin-orbit matrix is characterized by two parameters λ and λ' which refer to the splittings in the 3P manifold and the coupling between the 1P_1 and 3P_1 states, respectively. For atomic Cd, these parameters are found to be 1142 and 867 cm^{-1} , respectively, giving "unperturbed" atomic triplet and singlet limits of 31,256 and 43,664 cm^{-1} . The computed Cd_2 curves were shifted to reflect these asymptotes before obtaining the spin-orbit curves.

The calculated spin-orbit curves for Cd_2 are shown in Figures 3 and 4 and are labeled by the projection of the total angular momentum on the internuclear axis, parity and inversion. The spin-orbit curves are generally found to parallel the unperturbed curves, but there are several notable differences. There is a large avoided crossing induced between the attractive $1_g(^1\Pi_g)$ and repulsive $1_g(^3\Sigma_g^+)$ spin-orbit states. Moreover, the adjustment of the atomic asymptotes shows that the repulsive $^3\Pi_u$ state crosses the attractive $^1\Pi_u$ state near 2.9 Å and the spin-orbit coupling then induces an avoided crossing between the two 1_u states derived from the unperturbed states.

E. Cd_2 Fluorescence and Excited State Absorption

The family of Group II A and B metal dimers have attracted interest as possible high-power storage laser systems in analogy with the rare-gas excimers. The transitions of interest are the weakly forbidden bound-free bands arising from the bound curves that come from the $^1S + ^3P_1$ asymptotes and terminate on the dissociative ground-states. In the case of Cd_2 , the lowest $1_u(^3\Sigma_u)$ state has a small admixture of $^1\Pi_u$ (the coefficient of $^1\Pi_u$ in this state is 0.060 at 3 Å) and can thus radiate to the $1_g(^1\Sigma_g^+)$ ground-state. Using the computed $^1\Pi_u \rightarrow ^1\Sigma_g^+$ transition moment at 3.0 Å, we obtain a radiative lifetime of 24.4 μsec for the lowest 1_u state.

The visible fluorescence spectrum of Cd_2 has recently been measured by Drullinger and Stock.²¹ We have derived theoretical fluorescence intensities

from our calculated potential curves by a numerical evaluation of the bound-free Franck-Condon factors connecting the lowest 1_u state with the ground-state. The fluorescence intensity is given by the expression ²²

$$I(\omega)d\omega \sim \omega^3 \sum_v P_v |\langle \phi_v | u | \phi_\omega \rangle|^2$$

where the sum runs over the vibrational/rotational levels of the upper state (ϕ_v) whose populations are denoted by P_v , u is the $1_u \rightarrow 0_g^+$ electronic transition moment and ϕ_ω is the continuous, momentum normalized vibrational wavefunction for the lower state.

We assumed a Boltzmann distribution of vibrational levels and restricted the rotational quantum number to the most probable value at the temperature under consideration. Ten upper vibrational levels were included in the computation. The computed intensity at 675° K is shown in Figure 5. While the shape of the computed band is qualitatively similar to that measured by Drullinger and Stock, confirming the assignment to the lowest 1_u state, the computed curve peaks near 425 nm while the experimental curve has a maximum near 470 nm and is somewhat broader. This suggests an error in our computed binding energy of the $1_u ({}^3\Sigma_u)$ state of approximately 1/4 eV which is certainly plausible, considering the finite basis set used in the calculations.

Further insight into the $1_u \rightarrow 0_g^+$ fluorescence is gained by an examination of the contributions of the individual (thermalized) vibrational levels to the total fluorescence rate, shown in Figure 6. It is worth noting that near the peak intensity, the fluorescence is not homogeneous, being dominated by the $v = 0$ contribution. This might in principle, set limits on the rate at which energy could be extracted in a narrow band, the upper limit being determined by the collisional repopulation of the ground vibrational level. In this

connection, we note that the observed decay times²¹ are considerably longer than the 24.4 μsec radiative lifetime we calculate. The measured decay times undoubtedly reflect the rate of formation of the emitting species and do not represent pure radiative lifetimes.

Although the 1_u state we have been considering is the lowest radiating excimer level of Cd_2 , inspection of Figure 3 shows that there are three (0_g^+ , 0_g^- , 1_g) metastable levels that lie below this level which come from the unperturbed $3\Pi_g$ state and which raise the question of excited state-excited state absorption. Indeed, our calculations do show that there is a second bound $3\Pi_u$ state which dissociates to the $3P + 3P$ atomic levels (not shown in Figure 2) and lies 3.08 eV above the $3\Pi_g$ state at $R = 3 \text{ \AA}$, after proper adjustment of the asymptotes. This implies a strong excited state absorption near 403 nm, which falls well within our calculated 1_u fluorescence band and bodes ill for a projected Cd_2 laser operating on this band.

Concluding Remarks

Casual inspection of the potential curves of Zn_2 and Cd_2 suggests good qualitative agreement. However, a more detailed look, particularly at the spectroscopic constants, shows some serious discrepancies. Although it should be quite acceptable to use Zn_2 or Mg_2 potential curves as a rough guide to the laser spectroscopy of Hg_2 , there may be serious difficulties associated with quantitative predictions based on such a model.

Acknowledgments

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Table II. (15s 11p 7d) basis set of gaussian functions for the cadmium atom.

| Type | Exponent α | | |
|------|----------------------|--------|--------|
| s | 542 300. | p | 4050. |
| s | 81 360. | p | 956.4 |
| s | 18 670. | p | 307.6 |
| s | 5 360. | p | 114.4 |
| s | 1 782. | p | 45.86 |
| s | 657.0 | p | 16.96 |
| s | 257.6 | p | 7.058 |
| s | 78.08 | p | 2.181 |
| s | 35.01 | p | 0.7901 |
| s | 12.48 | p | 0.1174 |
| s | 6.039 | p | 0.0434 |
| s | 1.803 | | |
| s | 0.8094 | | |
| s | 0.1174 | | |
| s | 0.0434 | | |
| | d | 274.8 | |
| | d | 80.80 | |
| | d | 29.33 | |
| | d | 11.39 | |
| | d | 4.520 | |
| | d | 1.587 | |
| | d | 0.4758 | |

Table I. (13s 9p 5d) basis set of gaussian functions for the zinc atom.

| Type | Exponent α | | |
|------|----------------------|---------|---------|
| s | 207 699. | p | 1134.90 |
| s | 31 323.8 | p | 267.216 |
| s | 7 151.23 | p | 84.6060 |
| s | 2 034.51 | p | 30.6776 |
| s | 666.955 | p | 11.9956 |
| s | 241.327 | p | 3.7347 |
| s | 92.5665 | p | 1.2045 |
| s | 25.9066 | p | 0.1433 |
| s | 10.9332 | p | 0.0510 |
| s | 3.0046 | | |
| s | 1.1885 | | |
| s | 0.1433 | | |
| s | 0.0510 | | |
| | d | 56.0915 | |
| | d | 15.7455 | |
| | d | 5.3043 | |
| | d | 1.7697 | |
| | d | 0.5189 | |

Table III. Comparison between theory and experiment for the lowest atomic energy levels (in cm^{-1}) of zinc and cadmium. Note that for the 3P states the present nonrelativistic treatment does not distinguish fine structure components.

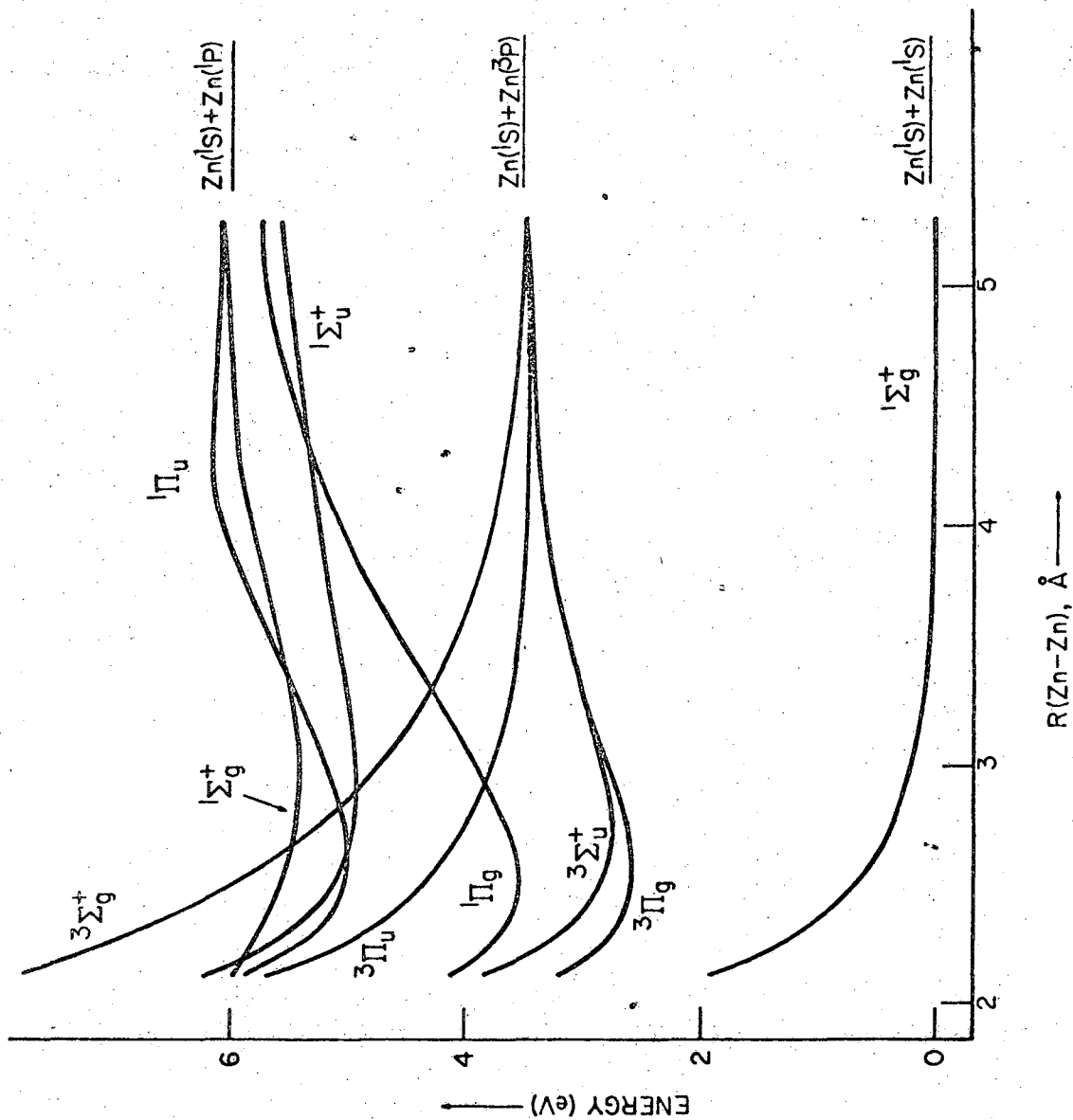
| Electronic State | Zinc | | Cadmium | |
|------------------|--------|------------|---------|------------|
| | Theory | Experiment | Theory | Experiment |
| 1S_0 ns^2 | | 0 | | 0 |
| 3P_0 $ns\ np$ | | 32,310 | | 30,110 |
| 3P_1 | 28,170 | 32,500 | 23,570 | 30,660 |
| 3P_2 | | 32,890 | | 31,830 |
| 1P_1 $ns\ np$ | 47,960 | 46,750 | 41,790 | 43,690 |

Table IV. Predicted spectroscopic constants for the bound states of Zn₂ and Cd₂ dissociating to ¹S + ³P and to ¹S to ¹P separated atom limits. Excitation energies T_e are given relative to two ground state metal atoms.

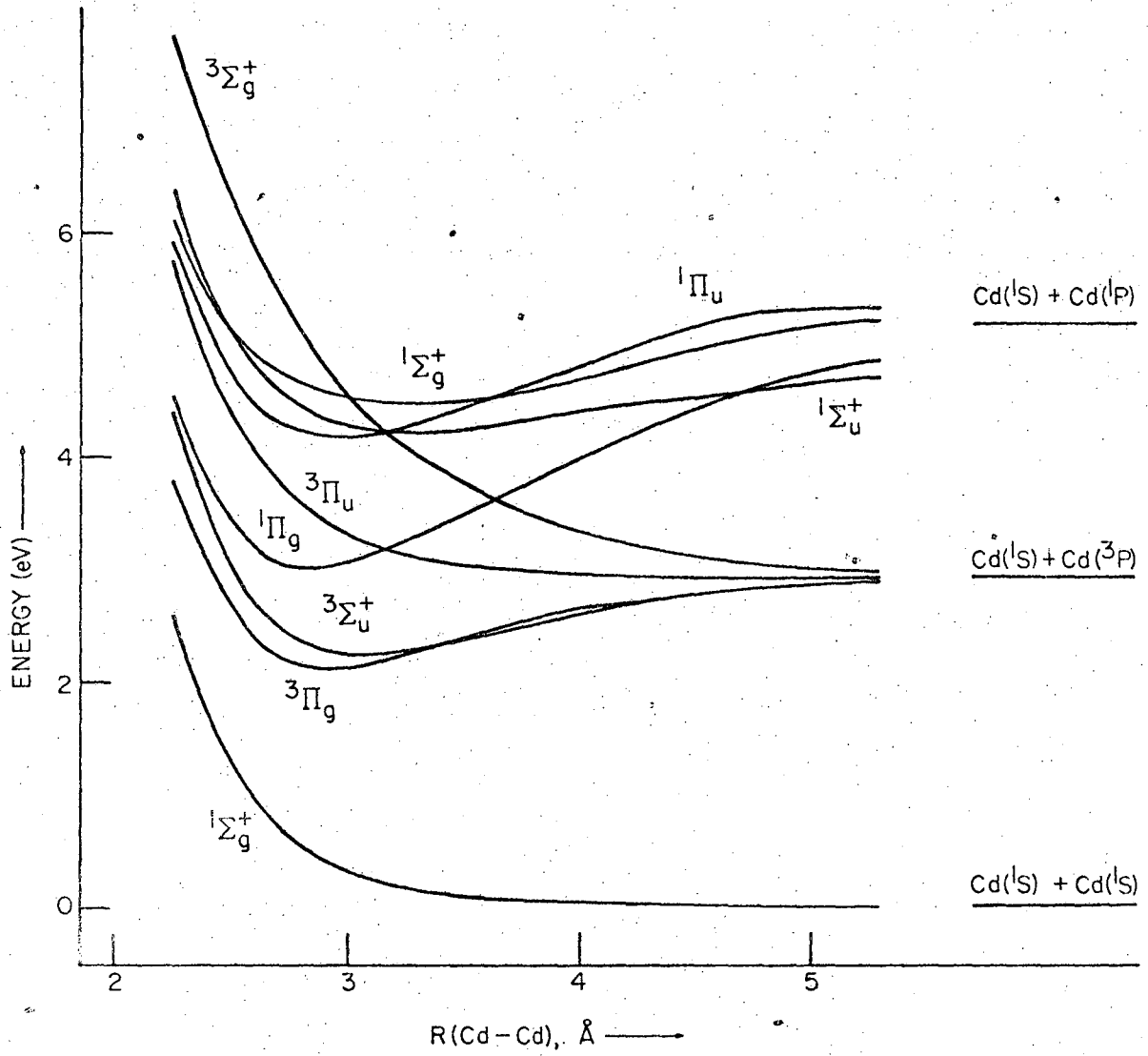
| | Electronic State | T _e (eV) | Adjusted T _e (eV) | r _e (Å) | D _e (eV) | ω _e (cm ⁻¹) |
|-----------------|--|---------------------|------------------------------|--------------------|---------------------|------------------------------------|
| Zn ₂ | 2 ¹ Σ _g ⁺ | 5.41 | 5.26 | 2.96 | 0.55 | 108 |
| | ¹ Π _u | 5.01 | 4.86 | 2.62 | 0.95 | 175 |
| | ¹ Σ _u ⁺ | 4.93 | 4.78 | 2.90 | 1.01 | 115 |
| | ¹ Π _g | 3.55 | 3.40 | 2.51 | 2.40 | 204 |
| | ³ Σ _u ⁺ | 2.75 | 3.31 | 2.73 | 0.74 | 154 |
| | ³ Π _g | 2.57 | 3.13 | 2.57 | 0.92 | 175 |
| Cd ₂ | 2 ¹ Σ _g ⁺ | 4.47 | 4.71 | 3.29 | 0.72 | 77 |
| | ¹ Σ _u ⁺ | 4.22 | 4.46 | 3.24 | 0.96 | 78 |
| | ¹ Π _u | 4.17 | 4.40 | 2.95 | 1.02 | 119 |
| | ¹ Π _g | 3.01 | 3.25 | 2.84 | 2.17 | 137 |
| | ³ Σ _u ⁺ | 2.23 | 3.18 | 3.06 | 0.70 | 104 |
| | ³ Π _g | 2.12 | 3.07 | 2.91 | 0.80 | 116 |

Figure Captions

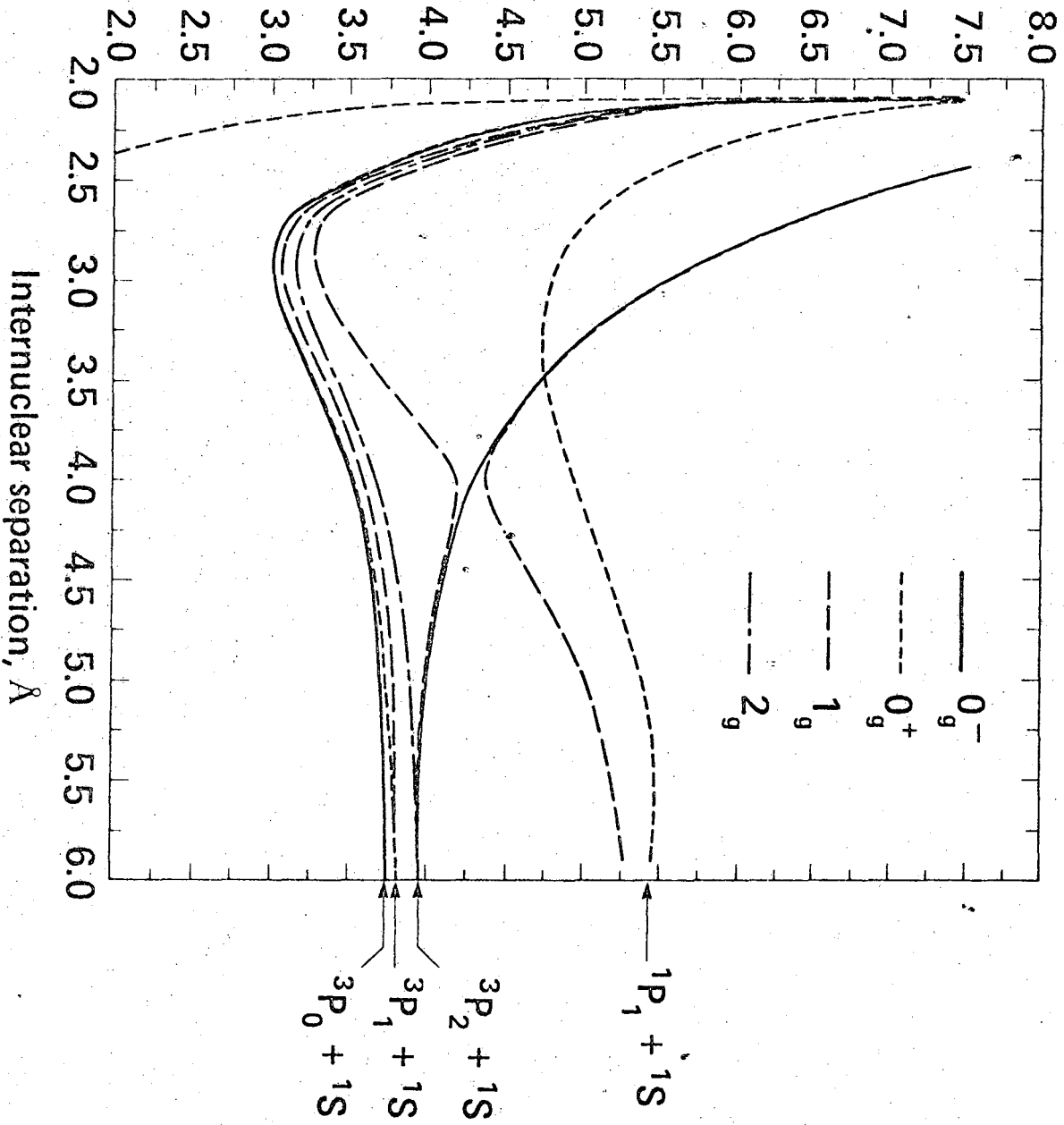
1. Theoretical potential energy curves for states of Zn_2 arising from $Zn(1S, 3P, \text{ and } 1P)$.
2. Theoretical potential energy curves for diatomic cadmium. All states of Cd_2 dissociating to $Cd(1S) + Cd(1S, 3P, 1P)$ are included here.
3. Gerade states of Cd_2 including spin-orbit coupling.
4. Ungerade states of Cd_2 including spin-orbit coupling.
5. Computed $Cd_2^* 1_u \rightarrow 0_g^+$ fluorescence band at 675°K, calibrated in relative units of quanta per unit wavelength per unit time.
6. Contributions of individual vibrational level to the Cd_2^* fluorescence rate at 675°K, in relative units of quanta per unit frequency per unit time.

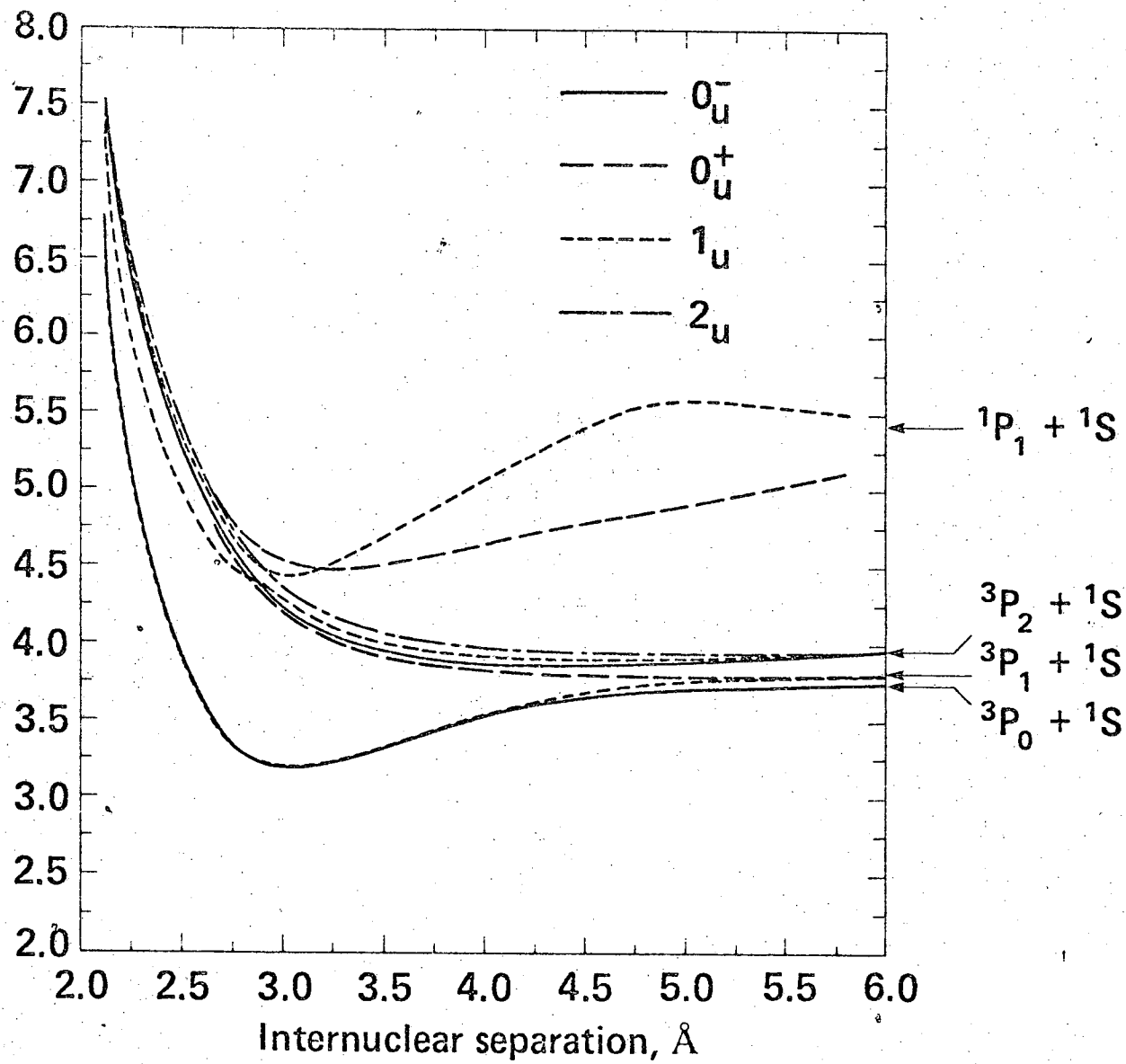


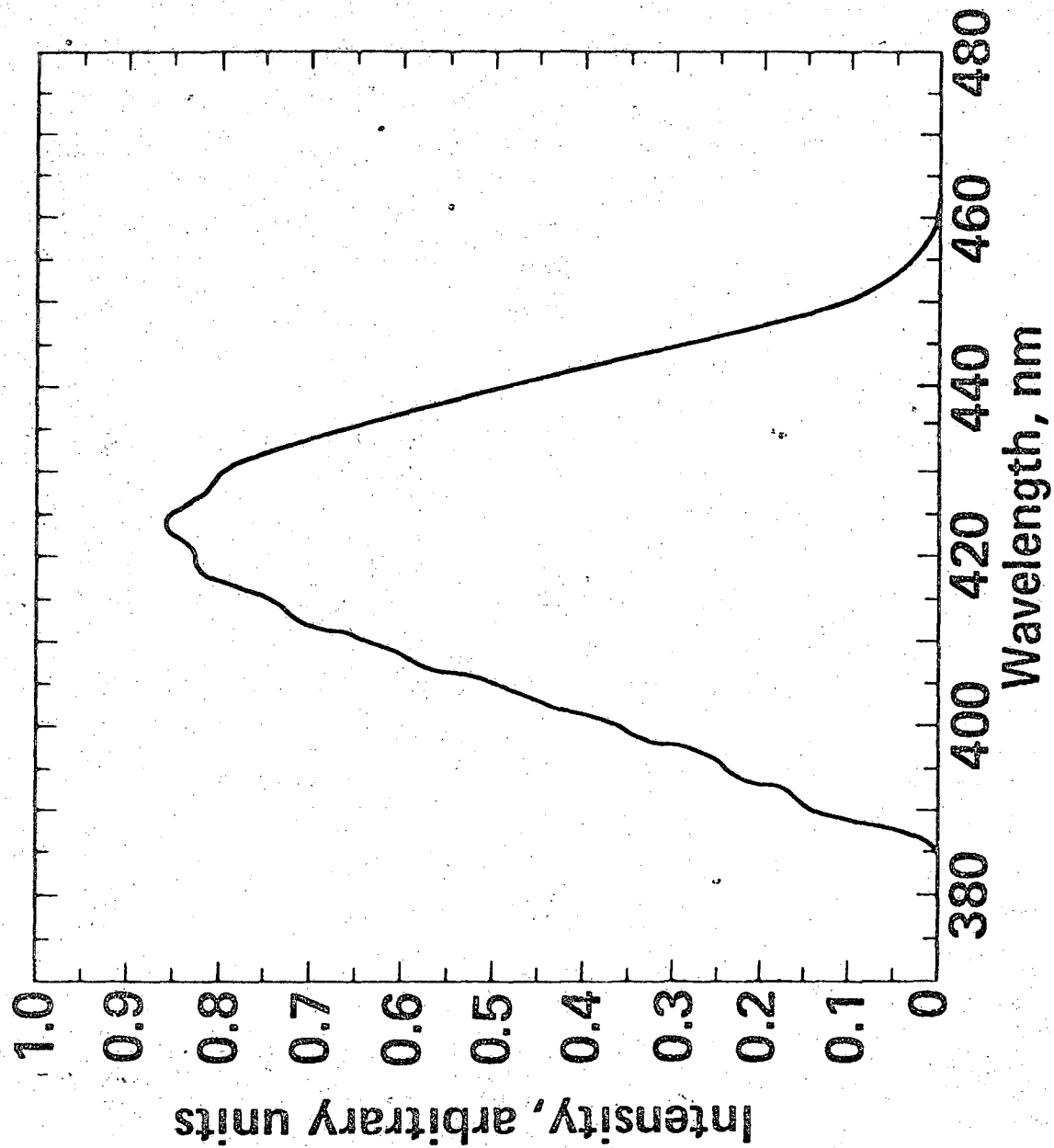
XBL 787-9778

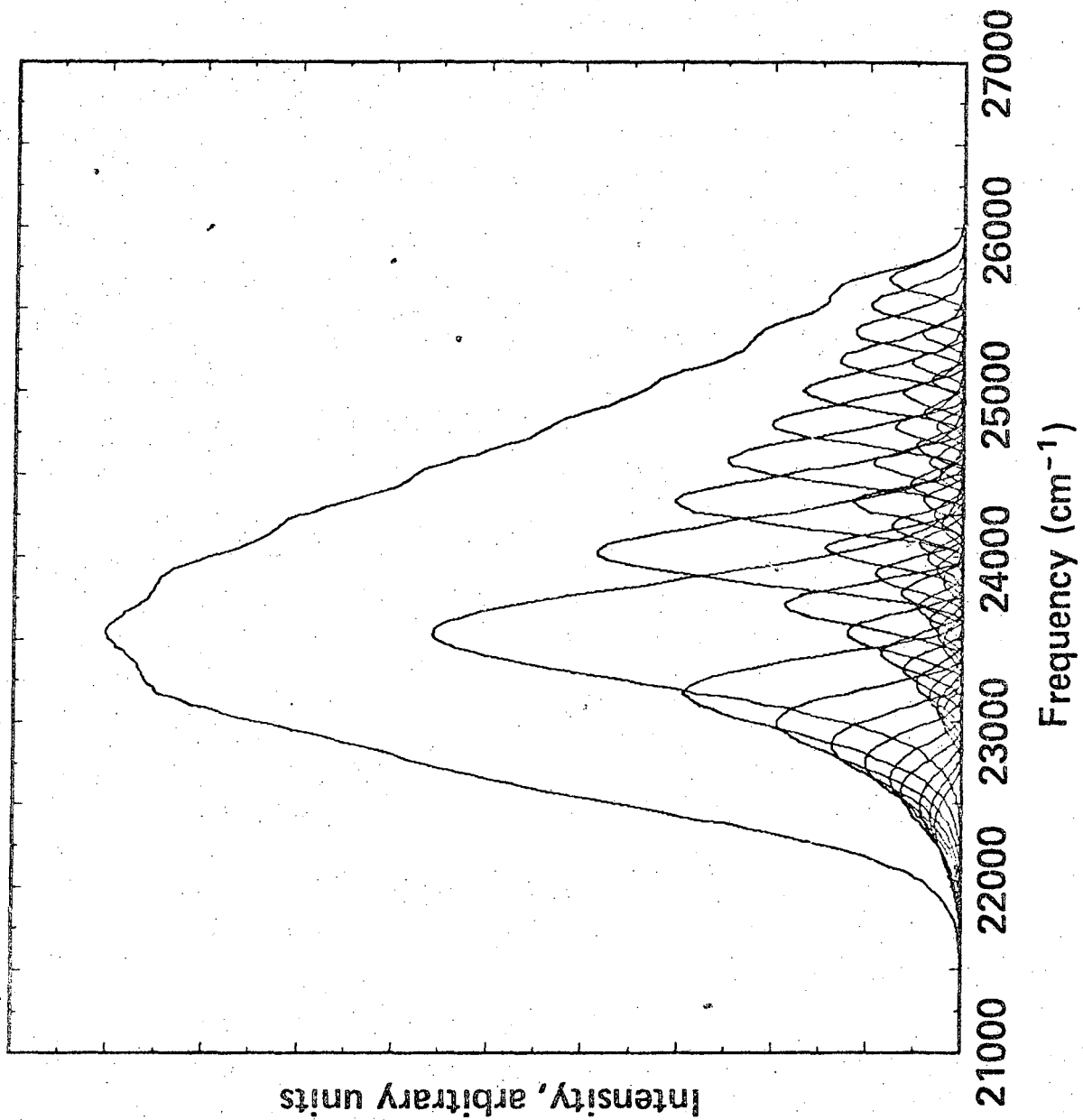


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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720