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J. Boatz, J. Sheehy, P. Langhoff "Monte Carlo Simulations of the Structures and Optical Absorption
Spectra of $AlAr_N$ Clusters" **HEDM Conference Presentation** (Statement A)

Monte Carlo Simulations of the Structures and Optical Absorption Spectra of AlAr_N Clusters

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Monte Carlo Simulations of the Structures and Optical Absorption Spectra of $AlAr_N$ Clusters

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ABSTRACT

Classical Monte Carlo simulation techniques have been used in conjunction with recently devised spectral methods for constructing the ground and low-lying excited state potential energy surfaces of atomic aggregates to predict the structures and optical absorption spectra of $AlAr_N$ clusters. The new spectral theory properly accounts for the change in electronic state character encountered in avoided crossings of diatomic adiabatic states and of the associated $AlAr_N$ aggregate states, in contrast to strictly pairwise-additive methods such as the Balling and Wright model, which constitute special limiting cases of the general spectral theory. The $AlAr_N$ simulations seek to understand several key issues regarding the experimental spectroscopic study of $AlAr_N$ clusters [James M. Spotts, Chi-Kin Wong, Matthew S. Johnson, and Mitchio Okumura, *Proceedings of the HEDM Contractors' Conference, 5-7 June 1996*], such as: (1) the location of the Al atom (surface or interior), (2) the role of the 4s and 4p states of Al in the putative 3p \rightarrow 3d transition, and (3) the origin of the spectral red shifts and splittings as a function of cluster size. In the case of the Al-Ar diatom, an avoided crossing between the π components of the 3d and 4p manifolds is expected to play a crucial role in the observed absorption spectra of $AlAr_N$ clusters. The (17s12p5d4f)/[7s6p4d3f] atomic natural orbital basis set of Widmark et al. (supplemented with diffuse (1s1p1d1f) functions), in conjunction with internally contracted multi-reference configuration interaction (MRCI) calculations from a [6331] (3e- in 13 orbitals) state-averaged complete active space reference wavefunction, was used to calculate the Al-Ar diatomic potential energy curves which correlate with the 3p, 4s, 3d, and 4p atomic states of Al. The Ar-Ar interaction energies were computed using the "HFDB2" potential of Aziz and Slaman. Detailed comparisons are made of the calculated spectra with the available measured data.

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SPECTRAL THEORY OUTLINE

Diatomic wavefunctions written as superposition of atomic product states (direct product of Al and Ar atomic states):

$$\begin{array}{cc} \text{Al} & \text{Ar} \\ \{3P, 4S, 3D, 4P\} \otimes \{1S_0\} \end{array}$$

$$\begin{aligned} \Phi &= \{ 3P_{+1} \bullet^1 S_0, 3P_0 \bullet^1 S_0, 3P_{-1} \bullet^1 S_0, 4S \bullet^1 S_0, 3D_{+2} \bullet^1 S_0, \dots, 4P_{-1} \bullet^1 S_0 \} \\ &= \{ 3P_{+1}, 3P_0, 3P_{-1}, 4S, 3D_{+2}, \dots, 4P_{-1} \} \end{aligned}$$

$$\Psi = \{ X \ ^2\Pi, A \ ^2\Sigma, B \ ^2\Sigma, \dots, (3) \ ^2\Pi \}$$

$$\Phi = U^t \Psi$$

Hamiltonian for atomic cluster given by:

$$H = \sum H^{(k)} + H^{(SO)}$$

$$H^{(k)} = D^t U^t E U D$$

$H^{(so)}$ = spin-orbit coupling operator for Al atom.

\mathbf{E} = diagonal matrix of diatomic interaction energies (X,A,B,C,... state energies)
 \mathbf{U} = unitary matrix which transforms from the diatomic basis to the atomic-product basis.
 \mathbf{D} = transformation matrix connecting the “rotated” and laboratory coordinate systems.

Atomic state mixing parameters U_{ij} obtained from eigenvectors of the diatomic and “spectral-product” transition moment matrices: $\mathbf{U} = \mathbf{U}_d (\mathbf{U}_{sp})^t$, where \mathbf{U}_d and \mathbf{U}_{sp} obey the following:

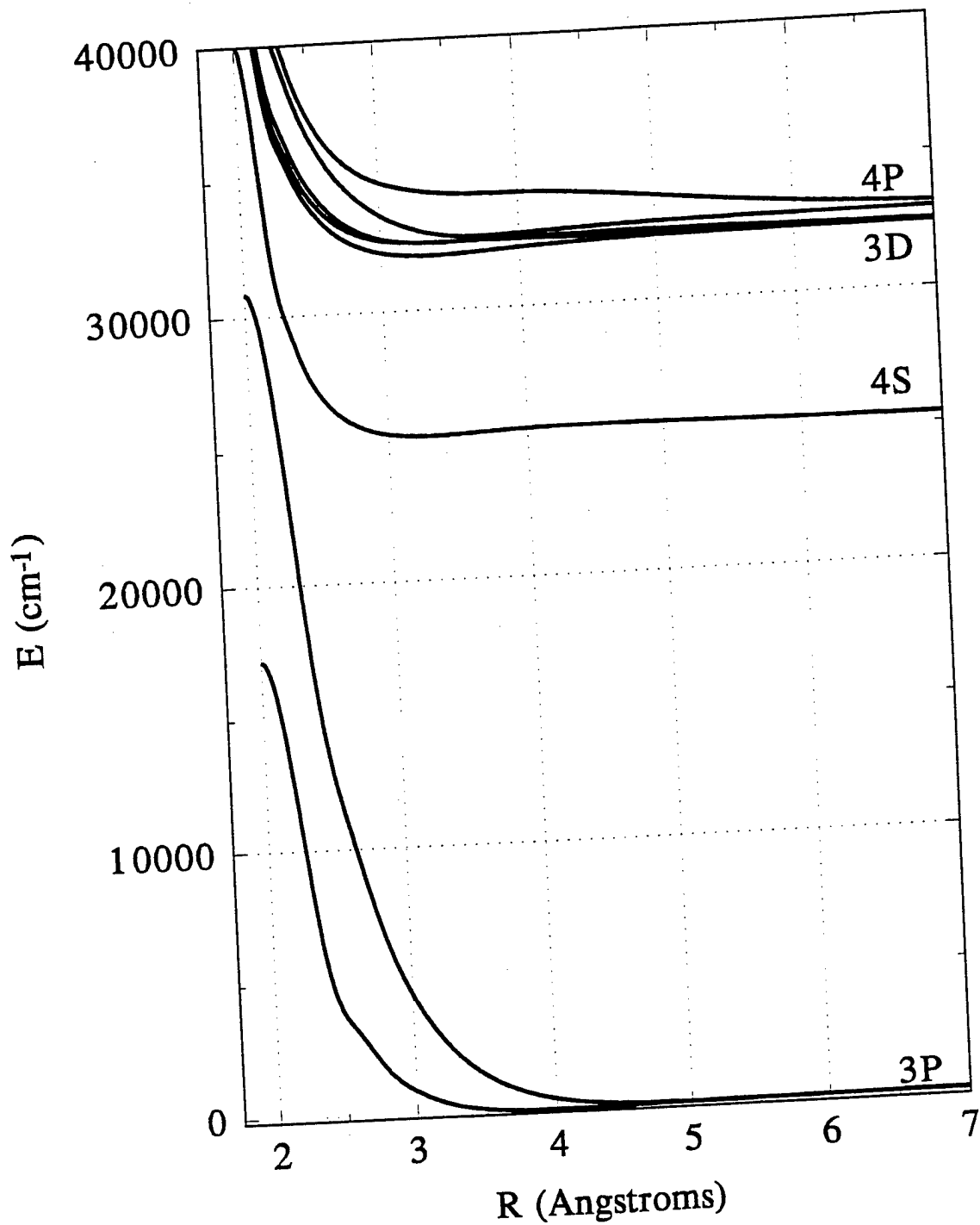
$$\lambda_d = (\mathbf{U}_d)^t \mu(\mathbf{R}) \mathbf{U}_d$$

and

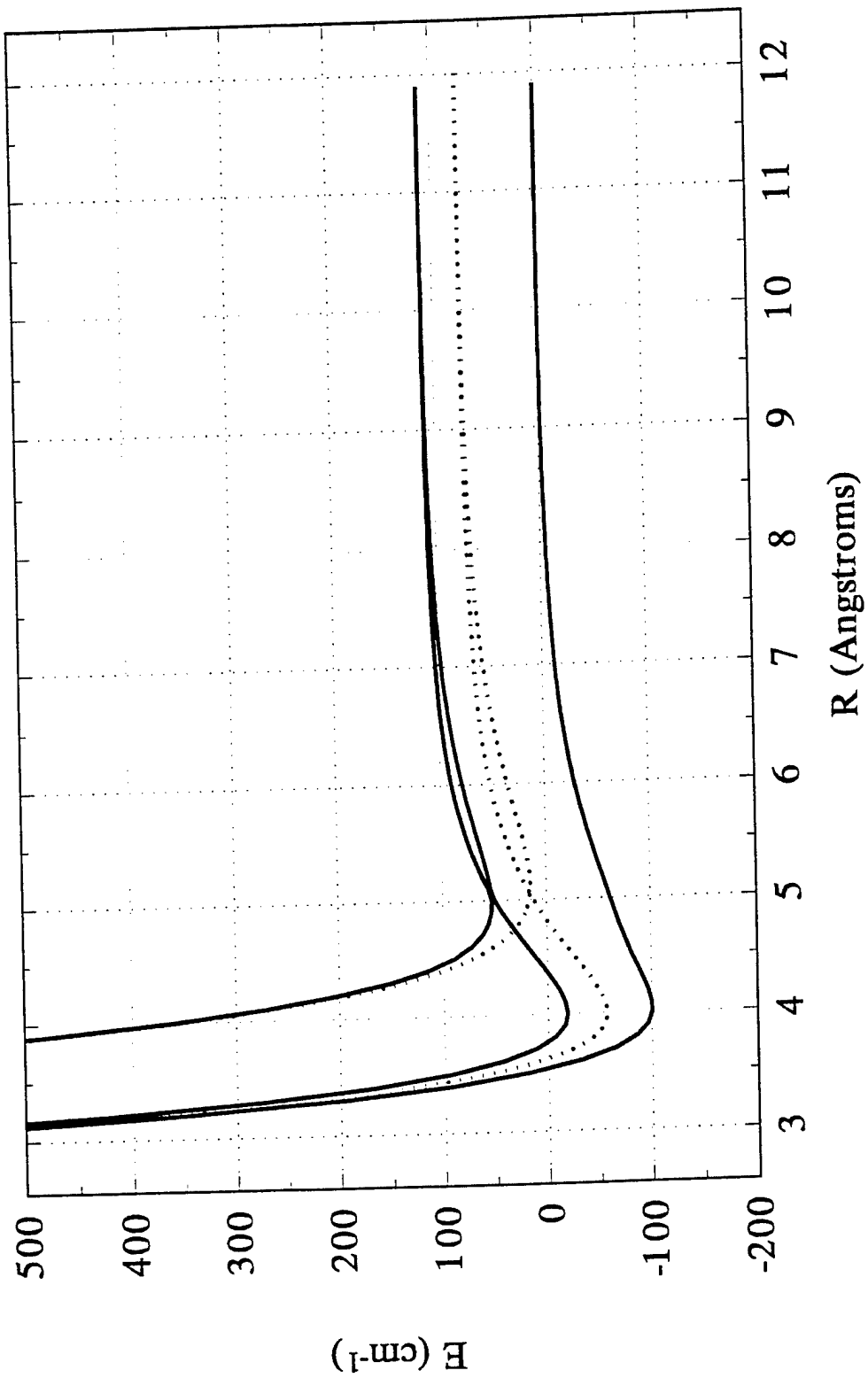
$$\lambda_{sp} = (\mathbf{U}_{sp})^t \mu_0(\mathbf{R} \rightarrow \infty) \mathbf{U}_{sp}$$

This is “exact” only in the case where $\lambda_{sp} = \lambda_d$.

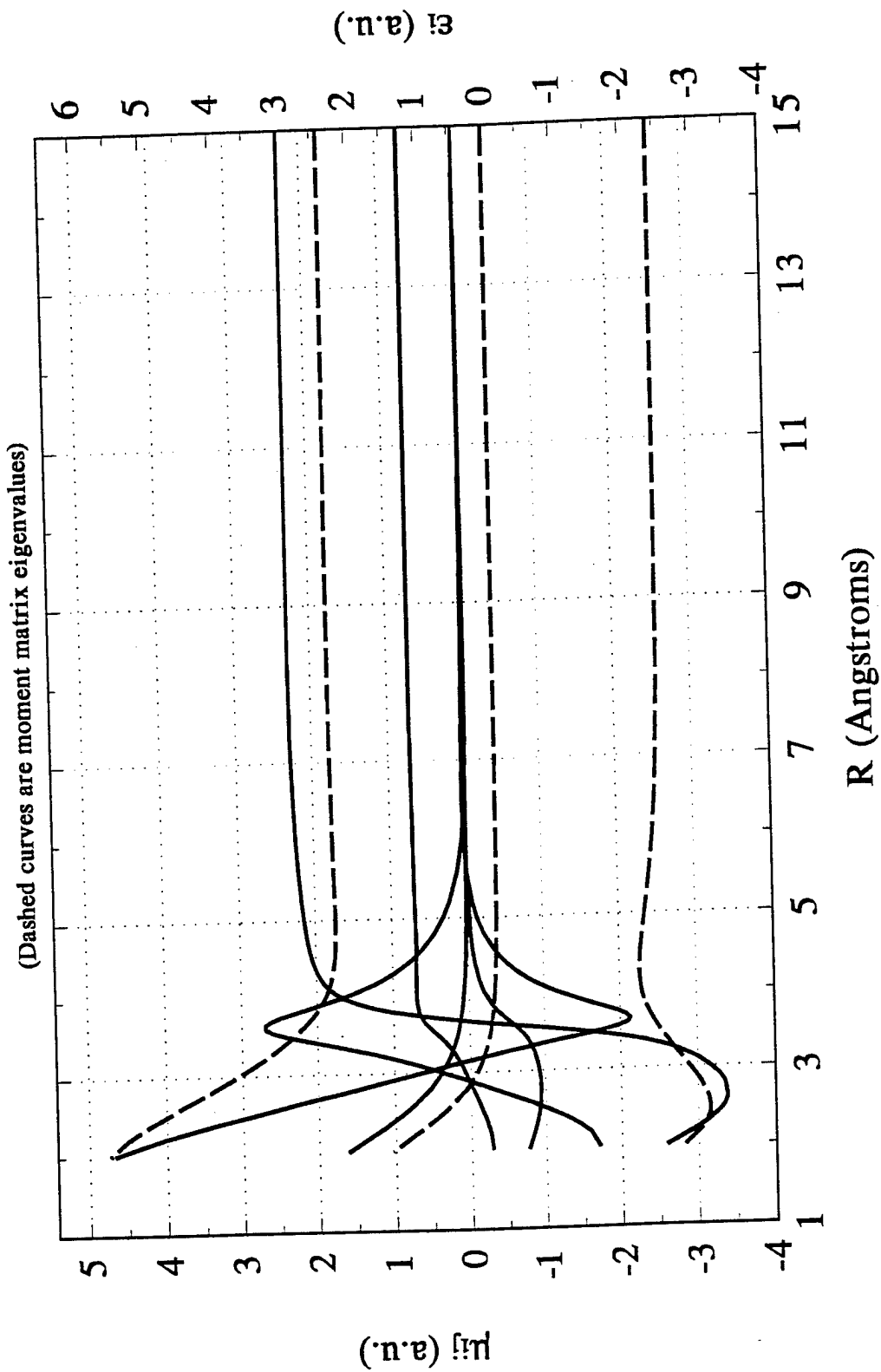
AlAr MRCI Potentials



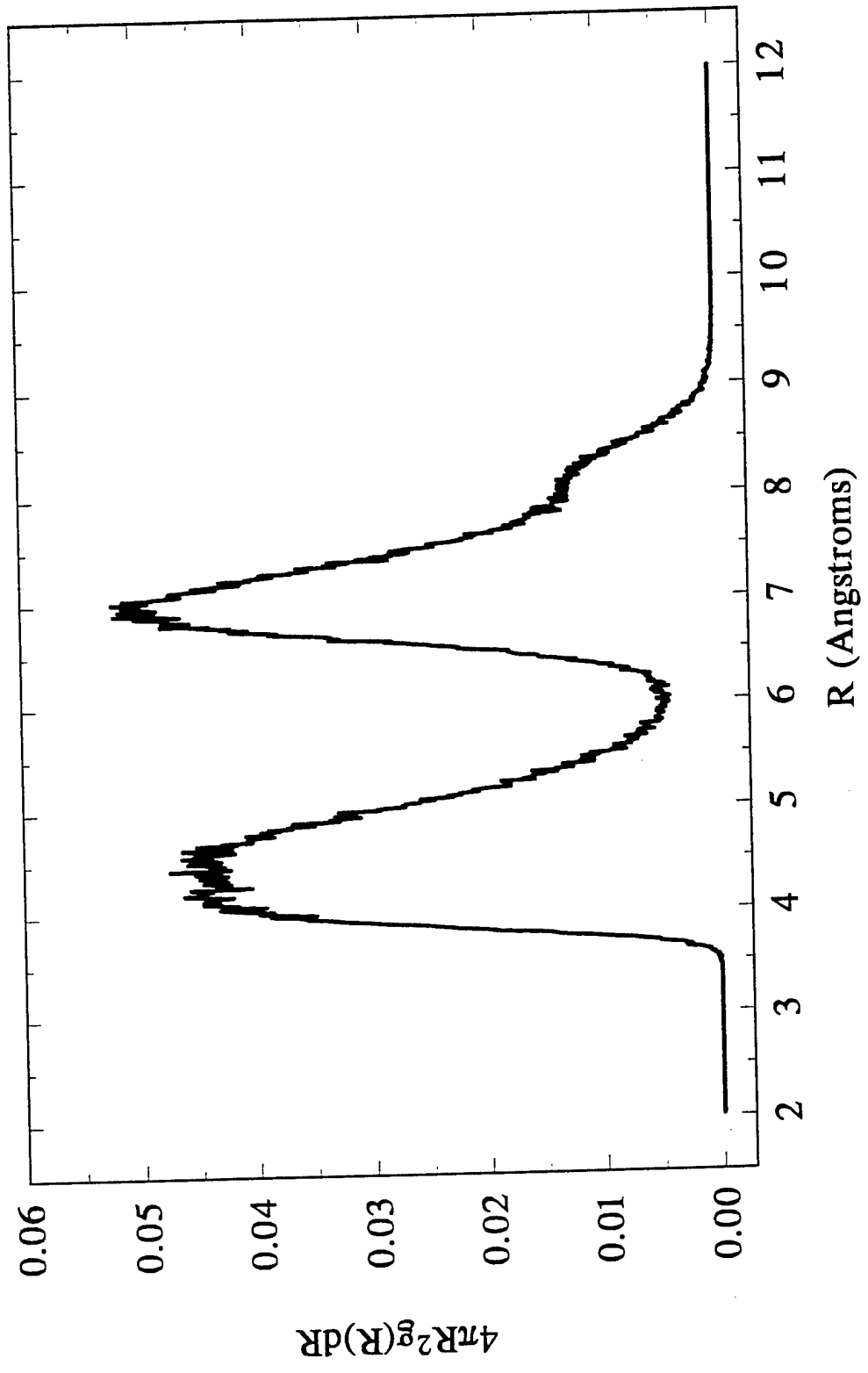
AlAr MRCI Potentials "3P" curves



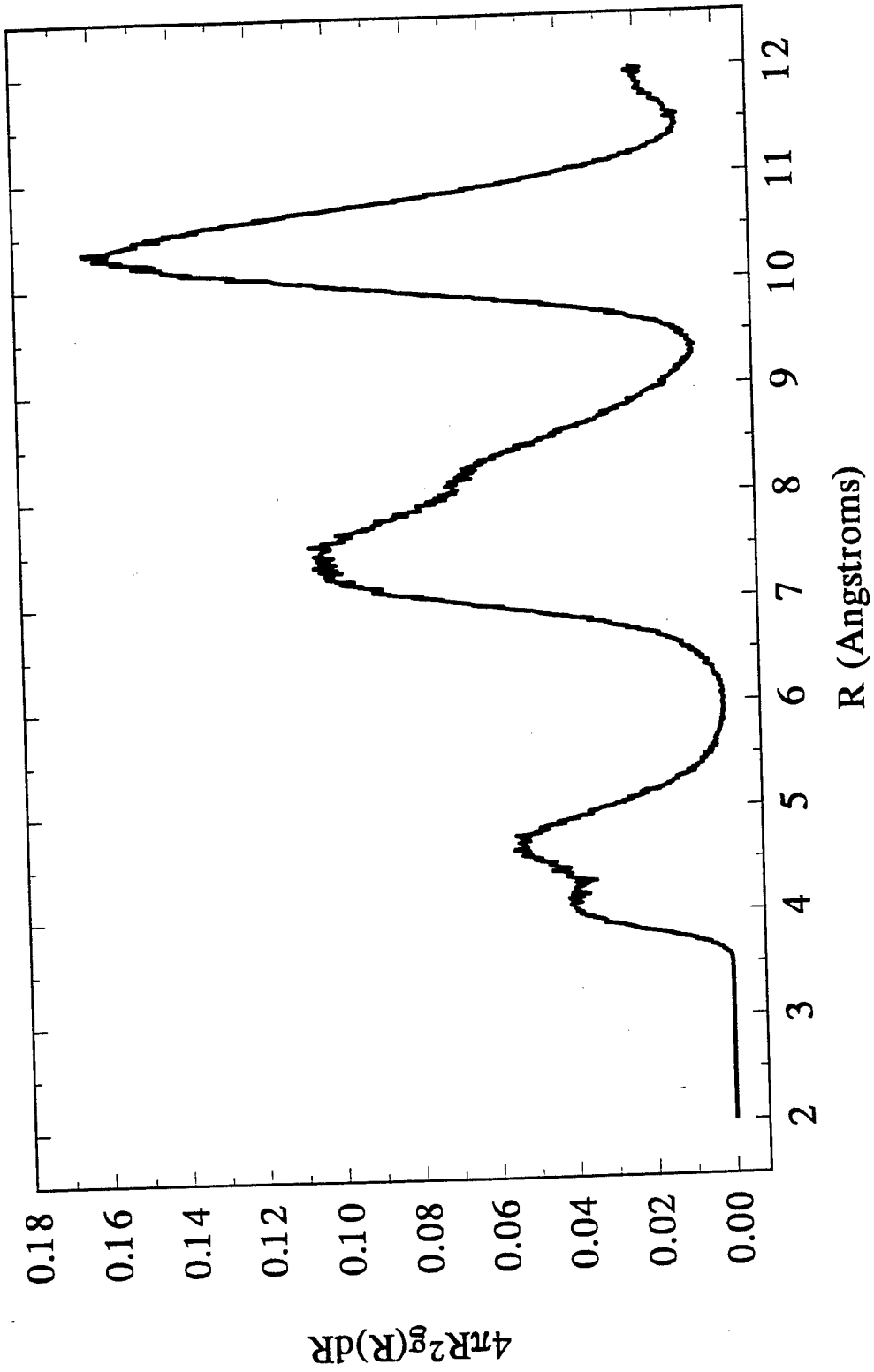
AIAt MRCI Transition and Dipole Moments $\Pi \rightarrow \Pi$ Moments



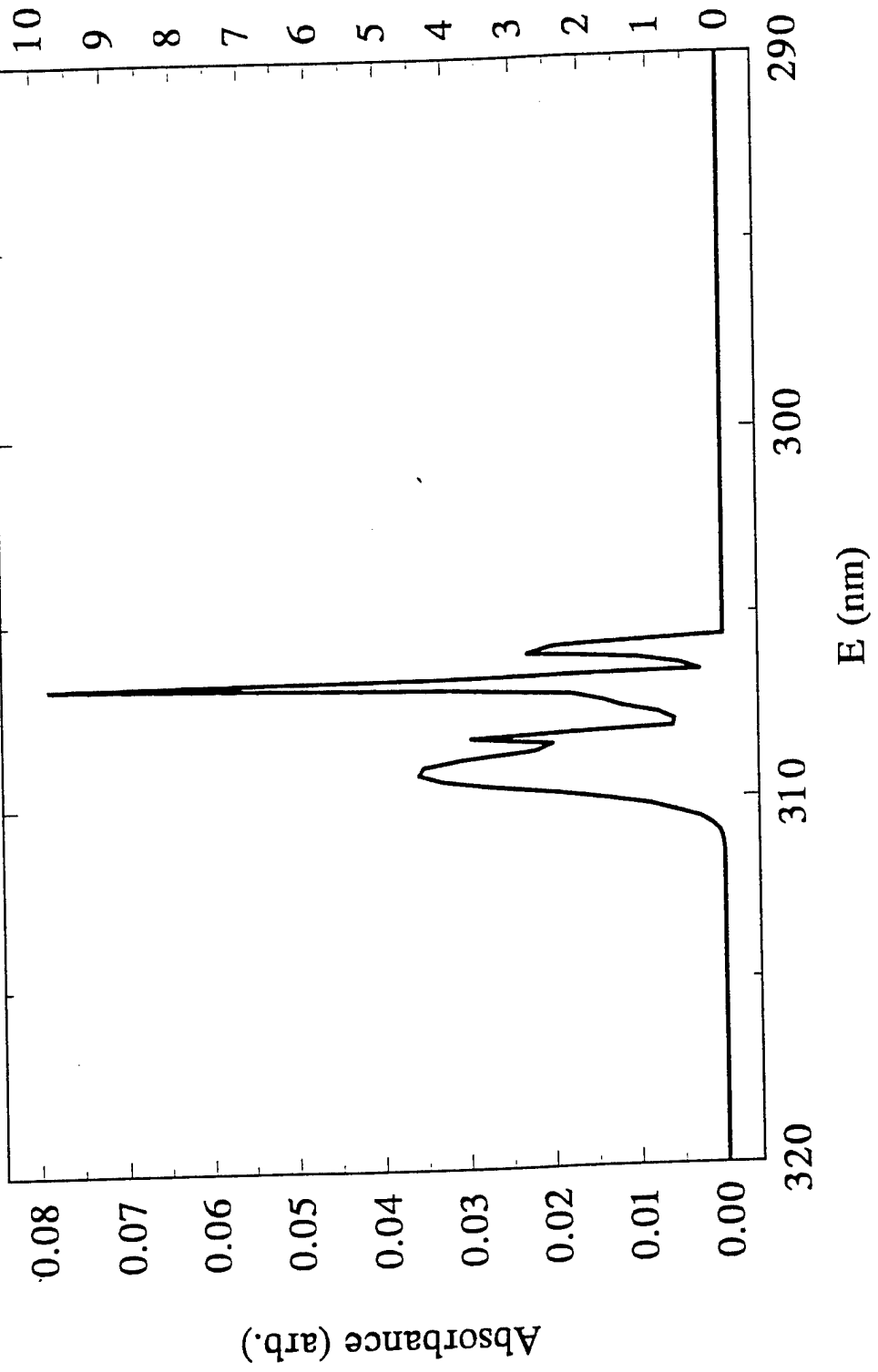
AlAr12 Radial Probability Distribution Function (RPDF)
T = 30K



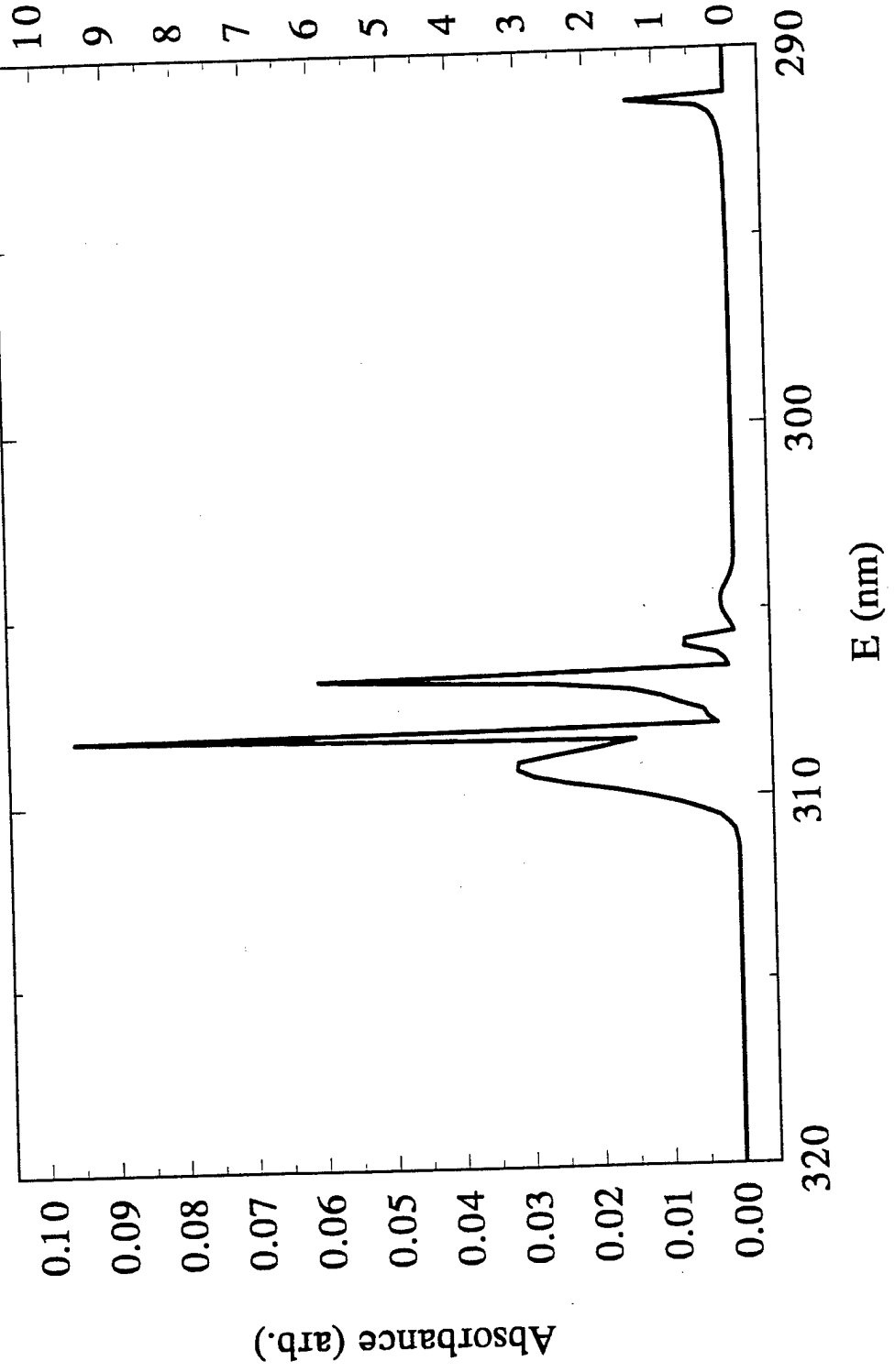
AlAr54 Radial Probability Distribution Function (RPDF)
T = 30K



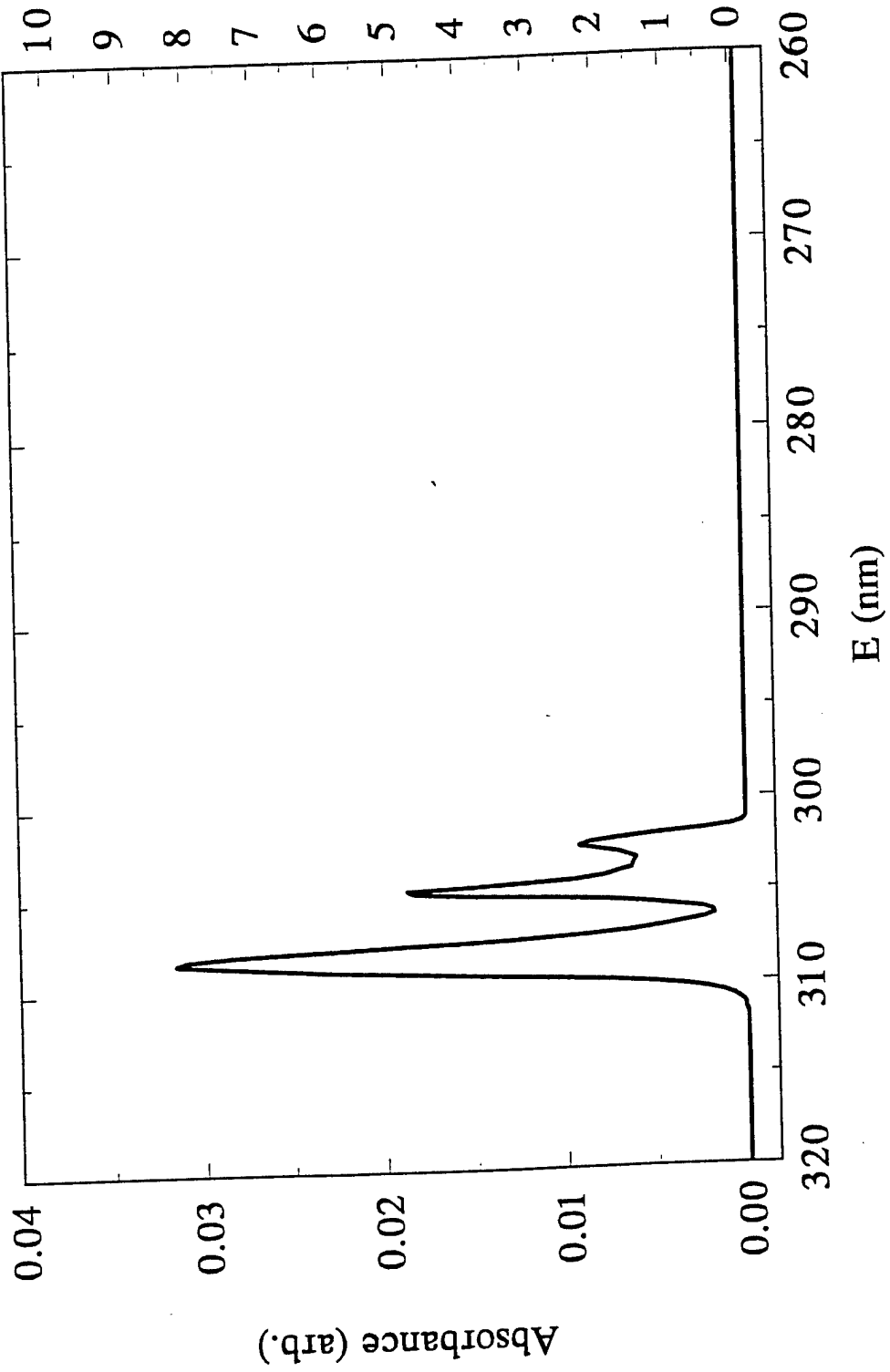
AlAr Absorption Spectrum
T = 20K, B&W limit



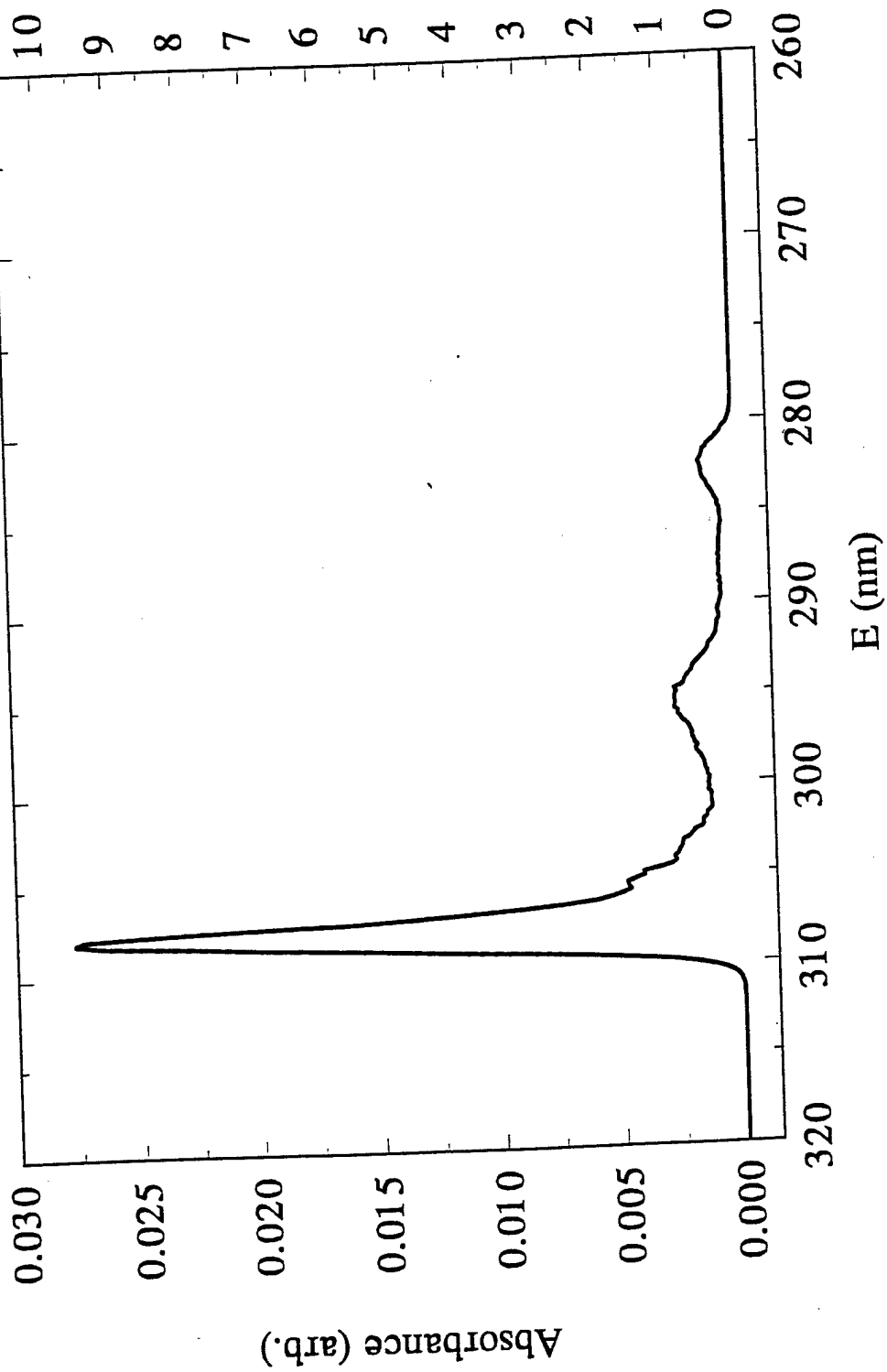
AlAr Absorption Spectrum
T = 20K, ST



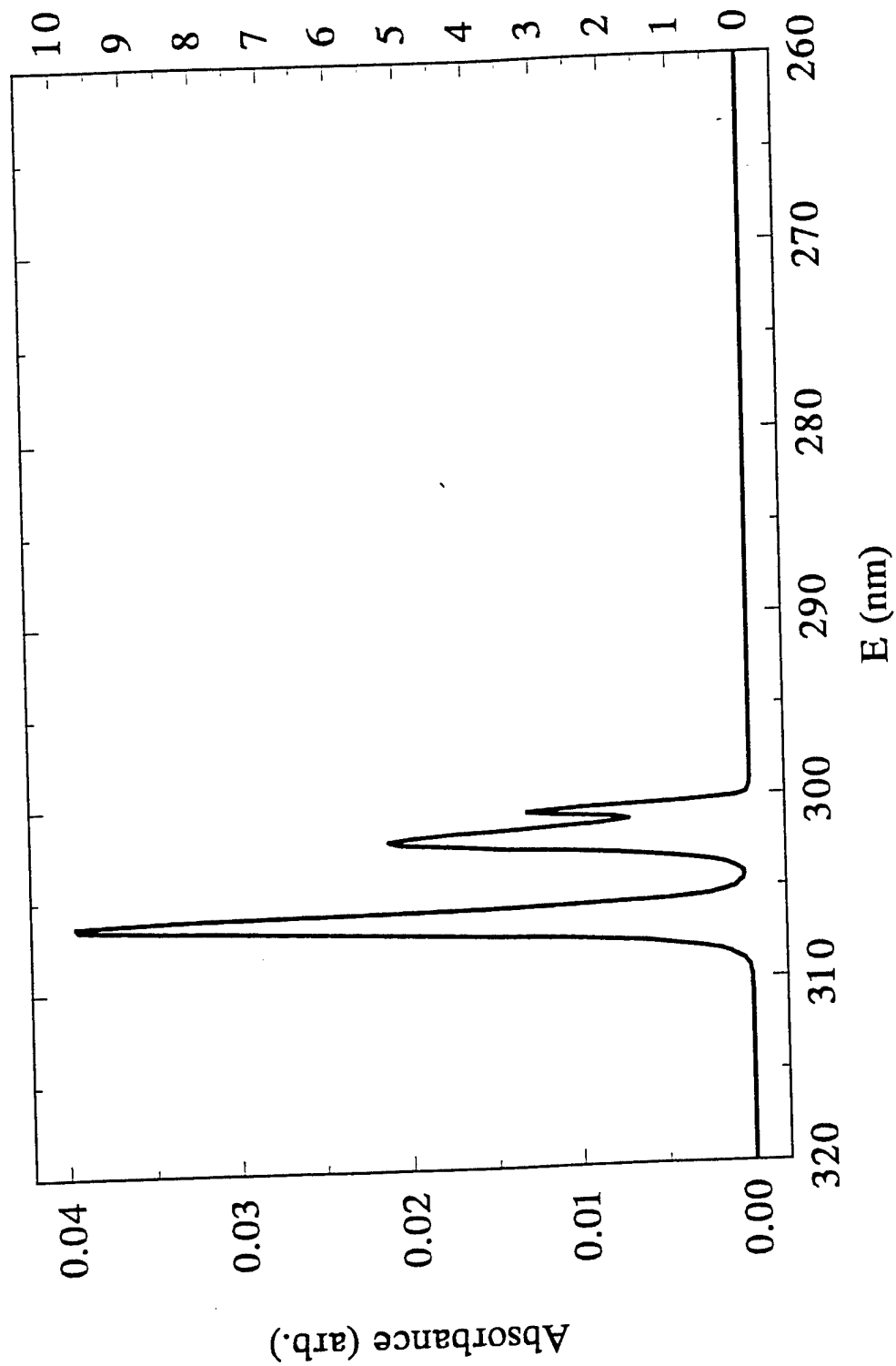
AlAr6 Absorption Spectrum
T = 30K, B&W limit



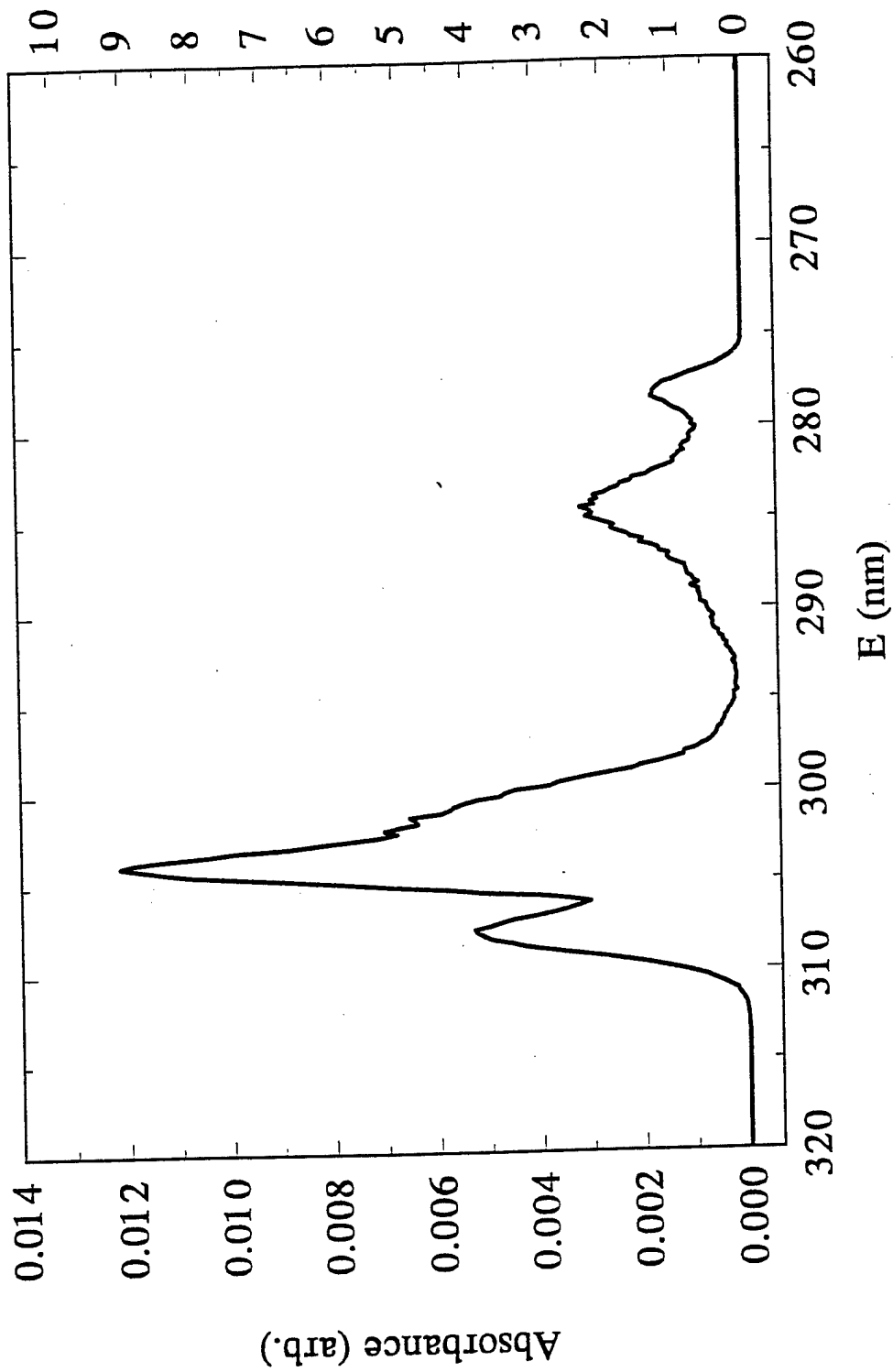
AlAr6 Absorption Spectrum
T = 30K, ST



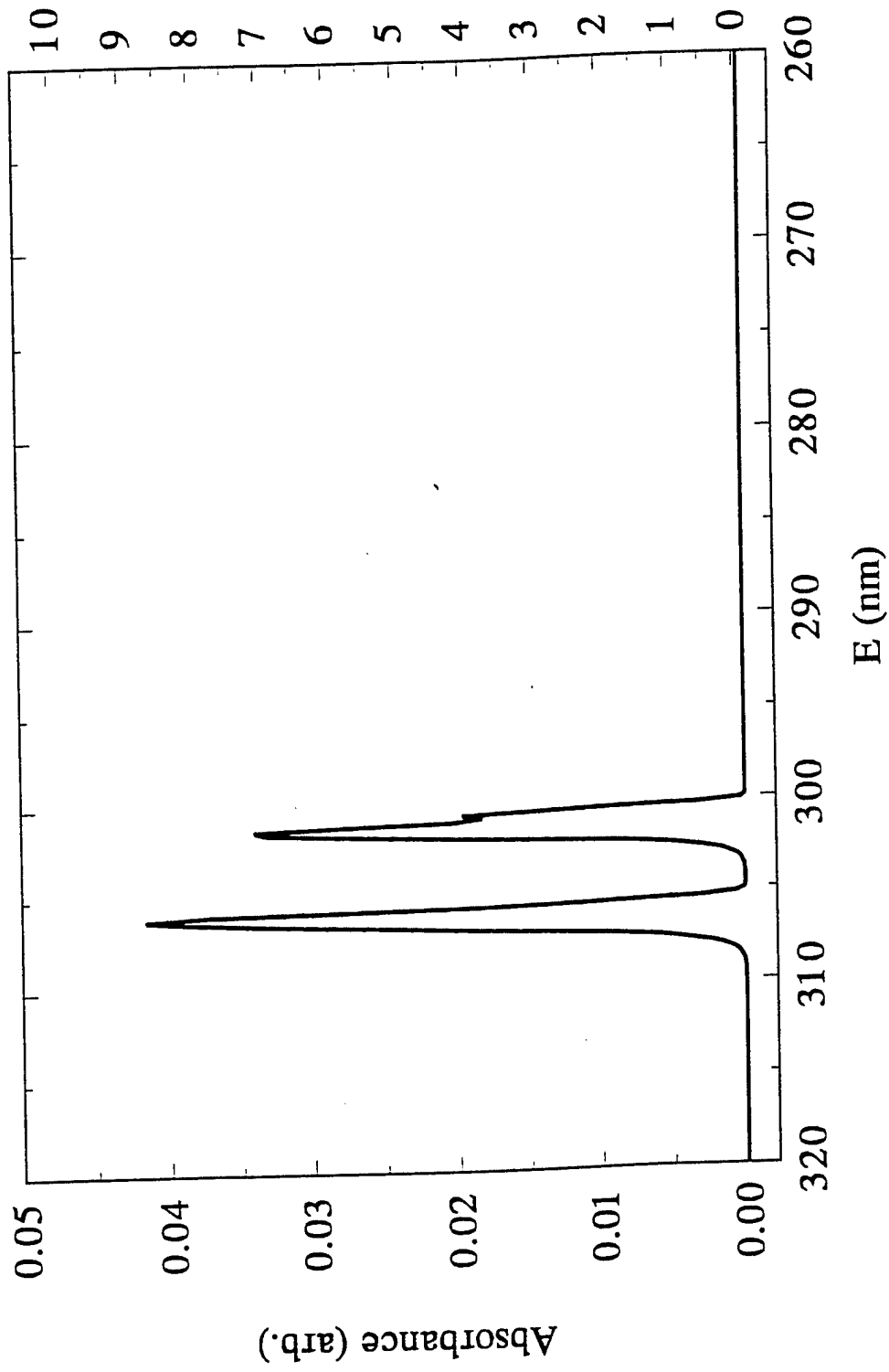
AlAr12 Absorption Spectrum
T = 30K, B&W limit



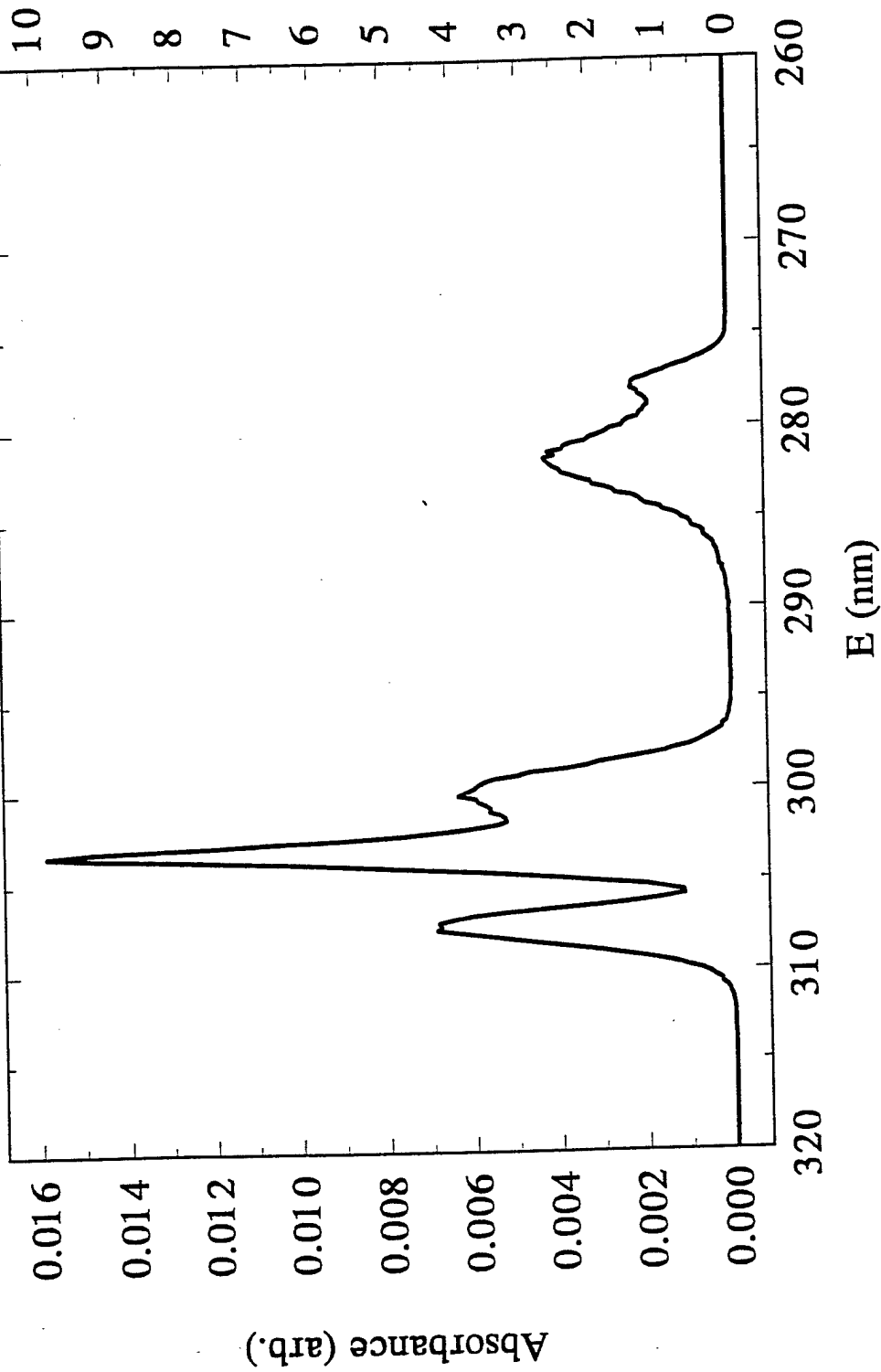
AlAr12 Absorption Spectrum
T = 30K, ST



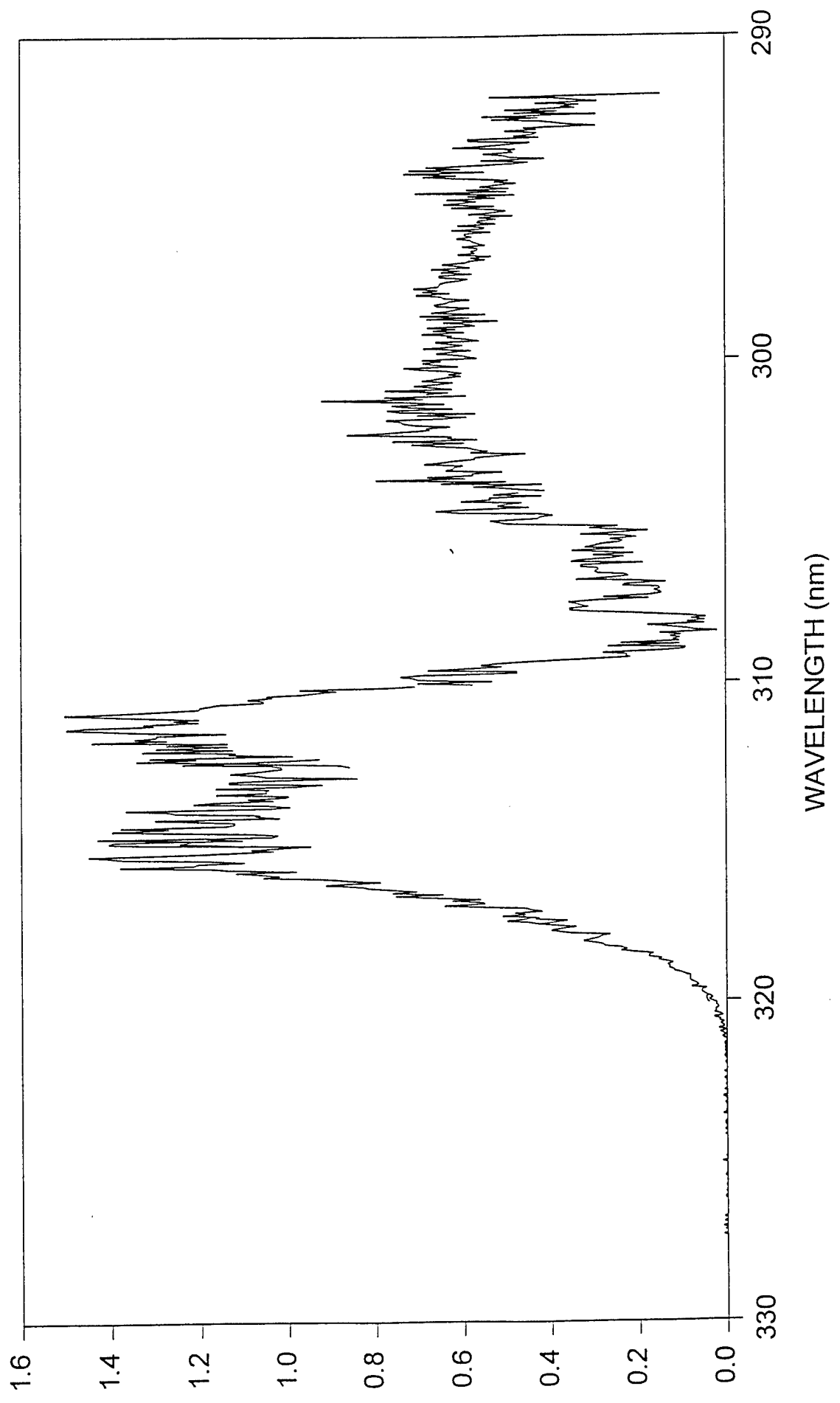
AlAr54 Absorption Spectrum
T = 30K, B&W limit



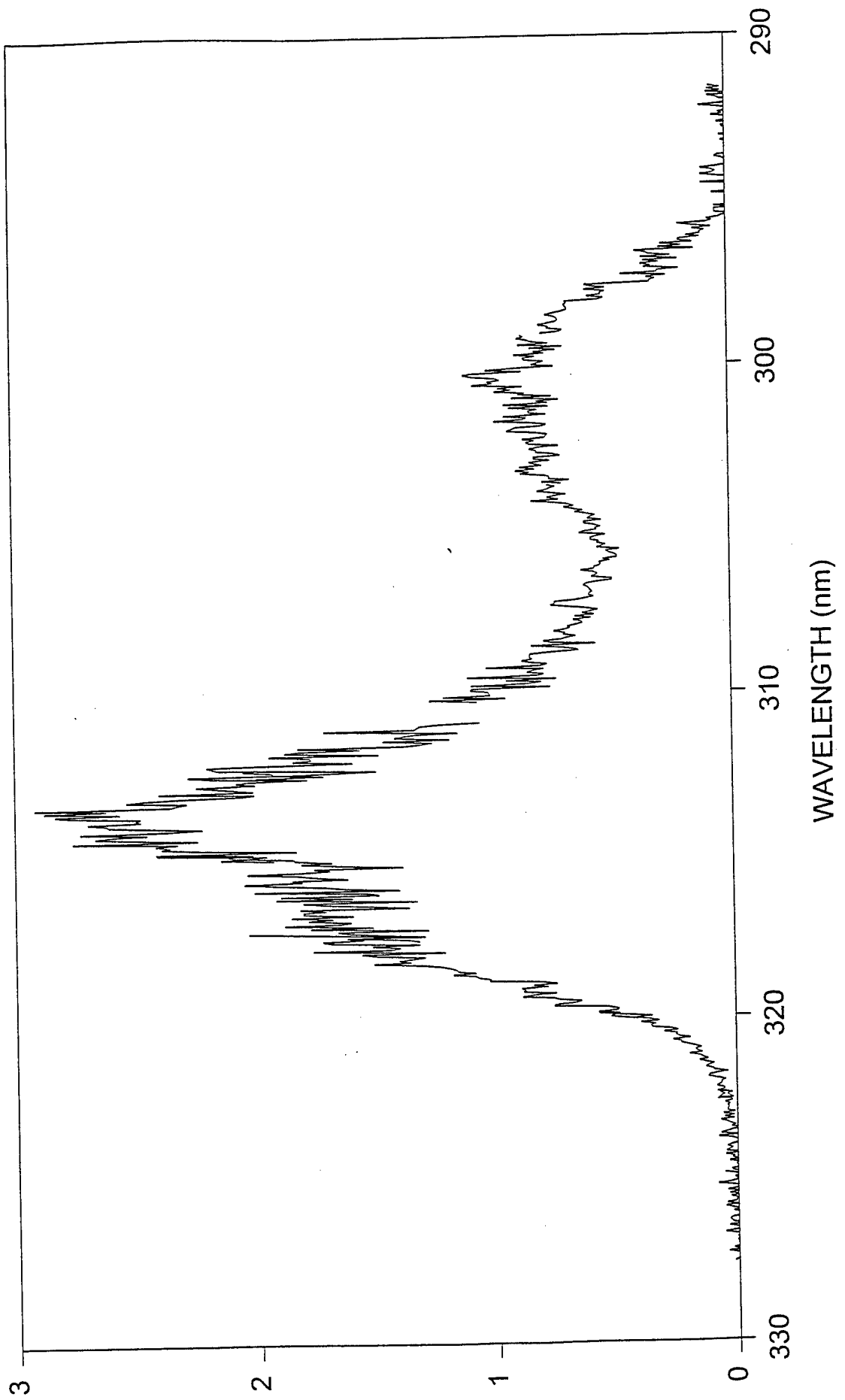
AlAr54 Absorption Spectrum
T = 30K, ST



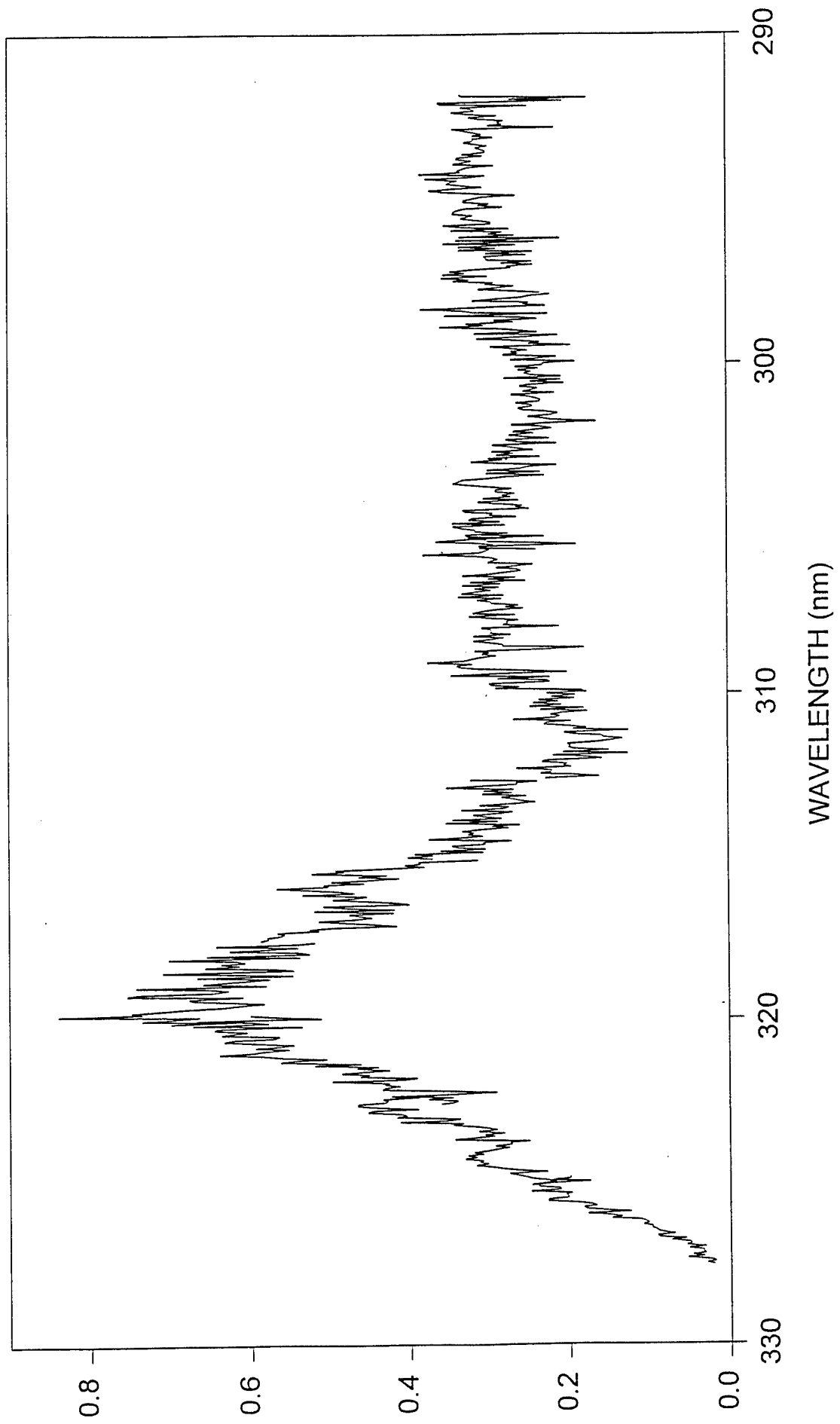
AlAr₆



AIAr₁₂



AIAr₅₄



CONCLUSIONS

1. Al is located on surface of clusters.
2. For AlAr, absorptions in the 311-306 nm range are due primarily to 3p \rightarrow 3d transitions. Absorption peaks at 305 and 292 nm are due to 3d \rightarrow 4p transitions.
3. In the B&W limit, the 3d-4p transitions are missing in the simulated spectra due to improper description of the avoided crossing between the 3d,4p Π states.
4. Simulated spectra do not reproduce observed red-shift in 3p \rightarrow 3d absorptions. This may be due to missing non-additive effects in the ground state potential energy surface of the clusters.

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