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# Absorption and emission spectra of matrix-isolated Ba atoms<sup>a)</sup>

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The absorption and emission spectra associated with the  $^1S_0 \rightarrow ^1P_1$  transition in group II atoms trapped in rare-gas matrices have been extensively studied,<sup>2-6</sup> but absorption and emission spectra for matrix-isolated Ba atoms have not appeared in the literature.

We report here our observations of white-light absorption bands associated with the  $6s\ ^1S_0 \rightarrow 6p\ ^1P_1$  transition of Ba atoms isolated in Ar, Kr, and Xe matrices at 10 K and the corresponding laser-excited emission bands for Ar and Kr matrices. The trapping sites for Ba in Xe proved to be highly unstable, and emission could not be observed. The apparatus used was similar to that described in Ref. 1, but the emission and absorption profiles were detected and recorded on an optical multichannel analyzer. Ba vapor was produced by heating Ba metal in a tantalum oven. The Ba vapor was mixed with a stream of rare gas and deposited on a sapphire plate attached to the cold finger of a liquid-helium cryostat. A tungsten lamp was used for the absorption measurements, and an  $N_2$  laser was used to indirectly excite the  $^1P_1 \rightarrow ^1S_0$  fluorescence.

The  $N_2$  laser wavelength of 3370 Å populated matrix-broadened higher-lying Ba energy levels, and the  $6p\ ^1P_1$  level was populated by lattice interaction and radiative cascade. This indirect excitation was convenient because the laser scatter could be easily filtered out of the fluorescence signal, the wavelength of which was essentially unshifted from the absorption-band wavelength.

We obtained stable sites for isolated Ba atoms in Ar and Kr matrices, but we were unable to do so for Xe matrices. As soon as the Ba-Xe system was exposed to white light for the transmission experiments the sites began to disappear, and exposure to laser light destroyed them immediately. As has

been pointed out by other workers,<sup>6</sup> the interaction of group II atoms and Xe atoms can be substantially stronger than for Ne, Ar, or Kr, and it may be that Ba-Xe chemical bonding prevents the formation of stable, isolated sites for Ba atoms.

The observed emission and absorption bands for Ba in Ar and Kr matrices are shown in Figs. 1 and 2, respectively, and the frequencies of the peaks for Ar, Kr, and Xe matrices are given in Table I. The results are quite similar to those obtained previously by other workers for Ca and Sr (see, for example, Ref. 2 and references cited therein). Although the absorptions in Ar appear to be a clear triplet, the enhanced central peak could be due to the overlap of two absorption doublets arising from distinct trapping sites. The absorption profile of Kr is quite suggestive of overlapping absorptions, as the peaks of the triplet are not evenly spaced and are of dramatically different widths. Because of the instability of the Xe trapping, we were unable to obtain a tracing of the absorption profile for Ba in Xe, but we measured the positions of the absorption peaks. The Ba-Xe absorption band was also a rough triplet, but the central peak was flat and twice as broad as the side peaks, again suggesting an overlap of two distinct bands.

It may be that the observed laser-excited fluorescence is from one of these sites only and that the emission from the other site is reabsorbed because it overlaps the absorption band. This possibility is indicated by the small secondary emission peak for Ba in Ar, which coincides with a minimum in the absorption band. Parenthetically we note that in previous, unpublished studies of matrix-isolated Ca and Sr in which we were able to work with more dilute samples, we clearly observed the absorption of the emission from one trapping site by the absorption band of another.

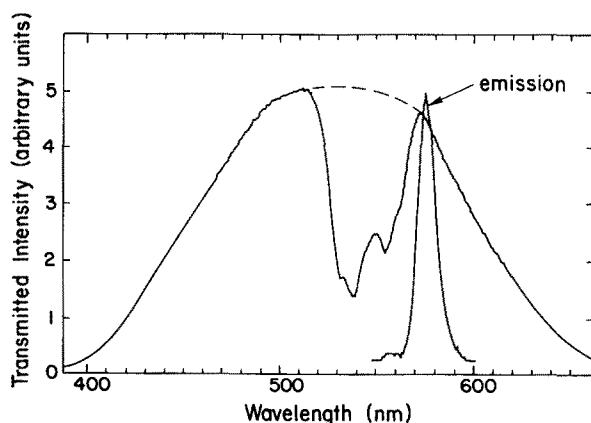


FIG. 1. The white-light absorption bands and  $N_2$  laser-induced emission associated with the  $6s\ ^1S_0 \rightarrow 6p\ ^1P_1$  transition of Ba atoms trapped in an Ar matrix at 10 K.

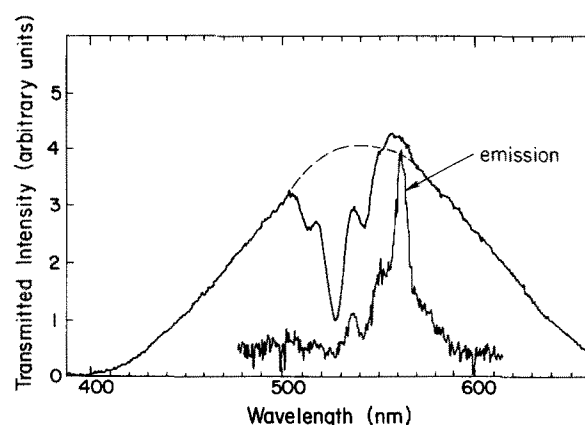


FIG. 2. The white-light absorption bands and  $N_2$  laser-induced emission associated with the  $6s\ ^1S_0 \rightarrow 6p\ ^1P_1$  transition in Ba atoms trapped in a Kr matrix at 10 K.

TABLE I. A summary of the white-light absorption peaks and laser-excited emission peaks associated with the  $6s\ ^1S_0 \rightarrow 6p\ ^1P_1$  transition in Ba in Ar, Kr, and Xe matrices at 10 K. The free atom transition occurs at 18 060  $\text{cm}^{-1}$ , and the matrix shifts of the absorption peaks from this value are also listed.

Matrix	Absorption peaks ( $\text{cm}^{-1}$ )	Matrix shift ( $\text{cm}^{-1}$ )	Emission peaks ( $\text{cm}^{-1}$ )
Ar	19 493 (100)	1433 (100)	17 606 (100)
	18 975 (100)	915 (100)	18 639 (100)
	18 433 (100)	373 (100)	
Kr	18 832 (100)	772 (100)	
	18 587 (100)	527 (100)	17 167 (100)
	18 018 (100)	- 42 (100)	
Xe	18 070 (100)	13 (100)	
	17 963 (100)	- 97 (100)	
	17 452 (100)	- 608 (100)	

Warm-up experiments yielded no additional information. No detectable shifts in the absorption or emission bands were observed with increasing sample temperature, nor was there a dramatic shift in the relative amplitudes of absorption peaks; the band structure simply faded away.

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## An exact asymptotic relation for the atomic and molecular wave function

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We begin by defining the coordinate system of interest. The Hamiltonian for an  $N$ -electron atom is

$$H' = \sum_{i=1}^N \left( -\frac{1}{2} \nabla_i^2 + \sum_{j<i}^N |\mathbf{r}_i - \mathbf{r}_j|^{-1} - \sum_{i=1}^N \frac{Z}{r_i} \right),$$

$$\nabla_i^2 \psi = \frac{1}{r_i} \frac{\partial^2(r_i \psi)}{\partial r_i^2} - \frac{\hat{L}_i^2 \psi}{r_i^2}, \quad H \psi_k = E_k \psi_k. \quad (1)$$

The radial distances are measured from a central nucleus of charge  $Z$ . We now perform a change of variables to the generalized hyperspherical coordinates defined by

$$\{\mathbf{r}_i\} \equiv \{r_i, \hat{\mathbf{r}}_i\} \rightarrow \{\xi_i\} \equiv \{R \xi_i, \hat{\mathbf{r}}_i\},$$

$$R^2 = \sum_{i=1}^N r_i^2, \quad (2)$$

$$\xi_i = \sin \alpha_N \cdots \sin \alpha_{i+1} \cos \alpha_i.$$

The quantities  $\alpha_i$  are generally called hyperspherical angles. In this coordinate system the Schrödinger equation becomes

$$-\left[ \frac{1}{2} \frac{\partial^2}{\partial R^2} - \left( \frac{3N-1}{2R} \right) \frac{\partial}{\partial R} - \frac{\hat{\Lambda}^2(\Omega)}{2R^2} + \frac{a}{R} \right] \Psi_k = E_k \Psi_k, \quad (3)$$

$$a = \sum_{i=1}^N \frac{Z}{\xi_i} - \sum_{i<j}^N (\xi_i^2 + \xi_j^2 - 2\xi_i \xi_j \cos \theta_{ij})^{-1/2}$$

$$\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_j = \cos \theta_{ij}.$$

The transformation  $\Psi_k = R^{-p} \Phi_k$  ( $p = 3N/2 - 1/2$ ) yields

$$\left[ -\frac{1}{2} \frac{\partial^2}{\partial R^2} - \left( \frac{\Lambda^2 + p(p+1)}{2R^2} \right) + \frac{a}{R} \right] \Phi_k = E_k \Phi_k, \quad (4)$$

$$\hat{\Lambda}^2 = \sum_{i=1}^N \left( \prod_{j=i+1}^N \sin^2 \alpha_j \right)^{-1} \left\{ \frac{\partial^2}{\partial \alpha_i^2} + [(3i-4) \cot \alpha_i - 2 \tan \alpha_i] \frac{\partial}{\partial \alpha_i} + \frac{\hat{L}_i^2}{\cos^2 \alpha_i} \right\}. \quad (5)$$

Note that the operator  $\hat{\Lambda}^2$  is a known grand angular momentum operator. Its eigenfunctions are the hyperspherical harmonics,

$$\hat{\Lambda}^2 Y_L(\Omega) = \lambda_L Y_L(\Omega) \quad \lambda_L = L(L+2-3N),$$

$$Y_L(\Omega) = Y_{L_i}^{m_i}(\hat{\mathbf{r}}_i) \prod_{j=2}^N Y_{L_j}^{m_j}(\hat{\mathbf{r}}_j) P_{L_j}^{L_j-1}(\alpha_j), \quad (6)$$

where  $L$  denotes the complete set of quantum numbers and  $P_{L_j}^{L_j-1}$  is constructed from Jacobi polynomials according to the prescription of Ref. 1.

We now wish to perform an asymptotic analysis on Eq. (4). Considerable interest has been generated in the asymptotic limits of wave functions and the electron density.<sup>2</sup> However, the problem is quite subtle and the published solutions have been criticized by various research groups.<sup>3</sup> The choice of hyperspherical coordinates yields one limit ( $R \rightarrow \infty$ ,  $r_i$  comparable) in a rather direct way. Thus one has only to decide which terms in Eq. (4) are dominant. The potential energy and eigenvalue terms are certainly important as  $R \rightarrow \infty$ . One can determine which of the first two kinetic terms may be dropped by a dominant balance agreement.<sup>4</sup> It is clear that the pseudoangular momentum term must be neglected so that ( $R \rightarrow \infty$ );

$$\left( -\frac{1}{2} \frac{\partial^2}{\partial R^2} + \frac{a}{R} \right) \Phi_k = E_k \Phi_k. \quad (7)$$