

Solvent shifts and excited-state potentials in rare-gas mixtures*

Michael J. Saxton

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Solvent shifts of the vacuum ultraviolet spectrum of xenon in gaseous argon are used to obtain the excited-state $\text{Ar}+\text{Xe}(^3P_1)$ potential. This potential is used to calculate the absorption and emission shifts of xenon in liquid argon, and satisfactory agreement with experiment is obtained. A new approximate scaling method is proposed to obtain the radial distribution function (rdf) for the mixture. This scaling uses readily available rdfs for hard sphere mixtures and pure fluids to obtain the rdf of the mixture. The emission and absorption shifts in the gas are sensitive to different regions of the excited-state potential, so that by combining observed shifts in absorption and emission one should be able to obtain accurate excited-state potentials.

I. INTRODUCTION

One of the simplest examples of a solvent effect is the shift in the electronic spectrum of an atom in solution from its gas-phase value. Most previous theories of solvent effects¹ have been based on dielectric continuum models, in which the solute is treated as embedded in a macroscopic dielectric; for a nonpolar system, only the dispersion energy is included. These theories predict a red shift, since the excited-state polarizability of the atom is typically larger than the ground-state polarizability, and the shift is just the average difference in dispersion energy in the ground and excited states.² But in some systems, for example xenon in argon, shifts to the blue are observed. In order to understand this effect it is necessary to take into account the repulsive part of the potential as well as the dispersion term.

An approximate expression for the shift $\Delta\nu = \nu_l - \nu_g$ in the center of the absorption band from gas (ν_g) to liquid (ν_l) is^{3,4}

$$h\Delta\nu = 4\pi\rho \int_0^\infty [V_e(r) - V_g(r)]g_{12}(r)r^2 dr, \quad (1.1)$$

where ρ is the number density of the solvent, $g_{12}(r)$ is the solute-solvent radial distribution function, and $V_e(r)$ [$V_g(r)$] is the pair potential between a solute and a solvent atom when the solute atom is in its excited [ground] state and the solvent atom is in its ground state. The important limitations of this formula are that the absorption is adiabatic, that the solute transition moment is unperturbed by the solvent, and that many-body forces can be neglected.³ The absorption process is assumed to occur so rapidly that the solvent structure surrounding the absorbing atom does not have time to rearrange. The pair distribution $g_{12}(r)$ is therefore taken to be the equilibrium distribution between the solute in its ground state and the solvent at the temperature and density of interest. We limit attention to the case where the absorbing solute is present in infinite dilution.

In this note we demonstrate that the simple expression Eq. (1.1) gives surprisingly good quantitative agreement with the observed blue shift in the xenon-argon system. In particular we show that (1) the formula gives a satisfactory picture of the observed blue shift in the dense

gas, where the measurements may be used to obtain information about the excited-state potential; (2) with knowledge of the excited-state potential obtained from the gas data it is possible to predict the observed blue shift in the liquid without use of any additional parameter; (3) the observed red shift in emission for the liquid is consistent with the prediction of Eq. (1.1).

In order to compute the shift it is necessary to know both the difference in potential $\Delta V(r) = V_e(r) - V_g(r)$ and the radial distribution function $g_{12}(r)$. Determination of these quantities is discussed in the following two sections.

II. DETERMINATION OF THE EXCITED-STATE POTENTIAL

For the ground-state potential $V_g(r)$ we use the Lennard-Jones potential of Hogervorst⁵: $\sigma_g = 3.65 \text{ \AA}$ and $\epsilon_g = 0.01534 \text{ eV}$.

Since the excited-state potential is not known, we assume it is a Lennard-Jones potential, and use two shifts measured in dense gas mixtures to obtain the potential parameters. For the $^1S_0 - ^3P_1$ line of xenon in argon, Rupin *et al.*⁶ report shifts of 0.0526 and 0.0958 eV, at argon densities of 300 and 400 amagat, respectively, and a temperature of 300 °K. From Eq. (1.1) and the appropriate low-density radial distribution function

$$g_{12}(r) = \exp[-V_g(r)/kT][1 + \rho \int dr_3 f_{13} f_{23}], \quad (2.1)$$

with

$$f_{mn} = \exp[-V_g(r_{mn})/kT] - 1, \quad (2.2)$$

we obtain the parameters for the excited-state potential: $\sigma_e = 4.133 \text{ \AA}$, $\epsilon_e = 0.0513 \text{ eV}$. From the scatter of $\pm 0.007 \text{ eV}$ in the observed shifts⁶ we infer an uncertainty of less than $\pm 0.016 \text{ \AA}$ in σ_e , while ϵ_e may vary between 0.02 and 0.07 eV. Numerical results indicate that the shift is much more sensitive to σ_e than to ϵ_e , so that measurements of blue shifts in gas-phase absorption spectra provide a sensitive probe of σ_e , but do not give an accurate determination of the well depth.

In Fig. 1, $V_e(r)$, $V_g(r)$, and $\Delta V(r)$ are plotted. We see

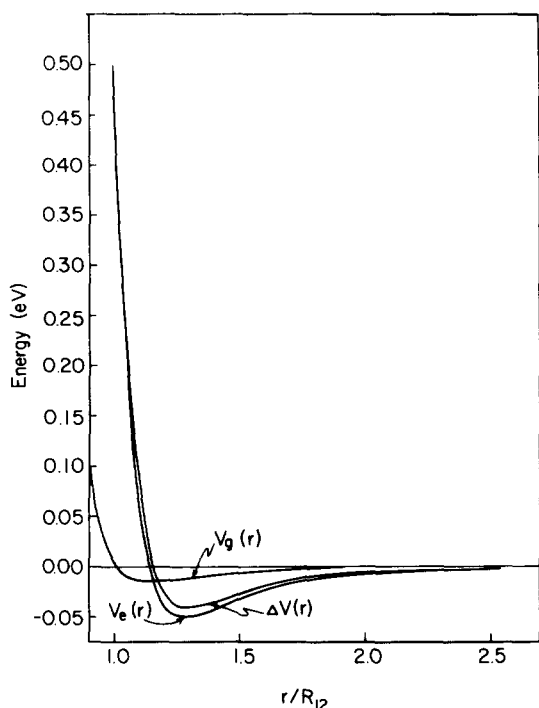


FIG. 1. The excited-state potential $V_e(r)$, the ground-state potential $V_g(r)$, and $\Delta V(r) = V_e(r) - V_g(r)$. The radius is given in reduced units r/R_{12} , where $R_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$.

that $\Delta V(r)$ depends much more strongly on the excited-state potential than on the ground-state potential.

Roncin⁴ has proposed a similar method of finding excited-state potentials using observed shifts in solid matrices. But this approach is based on the assumption that the guest atom is at a substitutional site in the matrix. Work on spectra of alkali metals in solid rare-gas matrices indicates that this assumption is not justified.⁷

III. DETERMINATION OF THE RADIAL DISTRIBUTION FUNCTION

The radial distribution function $g_{12}(r)$ for a mixture of Lennard-Jones particles has been calculated⁸ in the Percus-Yevick approximation, but not at the temperatures and densities we require. Rather than undertake an extensive calculation of $g_{12}(r)$, we propose a simple scaling method that permits us to use the more accessible results for hard-sphere mixtures, $g_{12}^{\text{HS}}(r)$. The radial distribution function for a mixture of hard spheres can be calculated readily in the Percus-Yevick approximation. These results cannot, however, be used directly since investigations of mixtures and pure liquids show that a hard-sphere radial distribution function gives an unrealistically high value of $g_{12}(r)$ near contact when compared to the correct value for a Lennard-Jones system.⁹ To correct this deficiency of $g_{12}^{\text{HS}}(r)$, we suggest the scaling rule, applicable to an infinitely dilute solution,

$$g_{12}(r, T, \rho) = [g(r, T^*, \rho^*) / g^{\text{HS}}(r, \rho_{\text{HS}}^*)] g_{12}^{\text{HS}}(r, \rho_{\text{HS}}^*). \quad (3.1)$$

We consider a Lennard-Jones mixture with potentials $V_{ij}(r)$ characterized by parameters σ_{ij} , ϵ_{ij} ($i, j = 1, 2$). In Eq. (3.1), $g_{12}(r, T, \rho)$ is the two-component radial distribution function for the Lennard-Jones mixture at tem-

perature T and density ρ ; $g(r, T^*, \rho^*)$ is the radial distribution function for a pure Lennard-Jones fluid with potential $V_{12}(r)$ at reduced temperature $T^* = kT/\epsilon_{12}$ and reduced density $\rho^* = \rho\sigma_{12}^3$; $g^{\text{HS}}(r, \rho_{\text{HS}}^*)$ is the radial distribution function for a pure reference hard-sphere fluid with hard-sphere radius $R_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$ and reduced density $\rho_{\text{HS}}^* = \rho R_{12}^3$; and $g_{12}^{\text{HS}}(r, \rho_{\text{HS}}^*)$ is the two-component radial distribution function for the reference hard-sphere mixture with hard-sphere radii σ_{11} and σ_{22} , and reduced density ρ_{HS}^* . The hard-sphere radii have been chosen so that for $r < R_{12}$, the hard-sphere radial distribution functions cancel, and the reduced variables have been chosen so that, in the low-density limit, $g_{12}(r) = g(r)$ for $r < R_{12}$ and the number of solvent atoms within $r < R_{12}$ is equal for $g_{12}(r)$ and $g(r)$. This scaling rule holds when the solvent-solute potential is not much different from the solvent-solvent potential, as can be seen from the definitions of $g(r)$ and $g_{12}(r)$.

The one-component radial distribution functions were taken from published tables,¹⁰ and the two-component hard-sphere radial distribution function was calculated by the method of Throop and Bearman.¹¹

IV. RESULT FOR THE ABSORPTION SHIFT

With these results we calculated the shift for xenon in liquid argon at a density of 713 amagat and a temperature of 105 °K. The calculated shift is 0.41 eV, and the observed shift¹² is 0.36 eV. The error limits obtained earlier for the potential give an error in the calculated shift of ± 0.16 eV. This agreement is quite satisfactory in light of the approximate nature of the radial distribution function and the use of the Lennard-Jones potential.

V. SHIFTS IN THE EMISSION SPECTRUM

This simple theory may also be used to explain qualitatively the shifts in the emission spectrum. The radius of an excited xenon atom is larger than that of ground-state xenon; $\sigma(\text{Ar-Xe}^*)$ is 4.13 Å while $\sigma(\text{Ar-Xe})$ is 3.65 Å. Since the lifetime¹³ of the 3P_1 state of xenon is 3.8×10^{-9} sec, the solvent atoms have time to readjust to the new electron distribution of the Xe^* . We therefore picture the emission process as occurring in an environment in which the solvent structure has come to equilibrium with the larger, excited xenon atom. The expression for the emission shift corresponding to Eq. (1.1) is

$$h\Delta\nu = 4\pi\rho \int_0^\infty [V_e(r) - V_g(r)] g_{12}^*(r) r^2 dr, \quad (5.1)$$

where $g_{12}^*(r)$ is the radial distribution function for an excited solute atom present in infinite dilution in the solvent.

Two problems suggest that it will be difficult to explain the emission shift quantitatively on the basis of the simple theory used above and the excited-state potential obtained from absorption measurements. First, the scaling procedure is less accurate, since the Ar-Xe* potential and the Ar-Ar potential are so different. Second, and more important, the shift in emission is much more sensitive than the absorption shift to the well depth.

One component radial distribution functions are not available for the reduced density appropriate for the emission measurements. Therefore we use the same

scaling as for absorption. We obtain a shift of -0.17 to -1.21 eV, and the observed shift¹⁴ is -0.12 eV.

In the dense gas, absorption shifts are about equally sensitive to the attractive part and the repulsive part of the excited-state potential, while emission shifts are significantly more sensitive to the attractive part compared to the repulsive part. Therefore it should be possible to construct an excited-state potential accurate in both regions by combining measurements of absorption and emission shifts. Unfortunately, emission shifts of xenon in dense gaseous argon have not been measured, so we cannot yet find a "best" excited-state potential.

Our consideration of the xenon-argon system suggests that shifts in the absorption and emission spectra of rare-gas liquid mixtures can be quantitatively explained by a simple theory in which repulsive forces play an important role. Furthermore, the simple scaling relationship we have proposed, Eq. (3.1), may be useful in other problems where crude values of $g_{12}(r)$ are acceptable. We emphasize, however that modern techniques^{9a,15} permit exceedingly accurate determinations of radial distribution functions if required, so that knowledge of this quantity is no longer a barrier to the interpretation of solvent shifts in simple fluid mixtures.

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