Absorption Spectra of Some Liquids in the VUV

Vladimir O. Saik and Sanford Lipsky*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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Absorption spectra and oscillator strengths have been determined for the liquids, benzene, toluene, hexafluorobenzene, tetramethylsilane, 2,2-dimethylbutane, and 2,2,4-trimethylpentane over a spectral range from 120 to 300 nm and compared with gas phase spectra. The effect of condensation manifests itself most obviously for transitions assigned to upper states of relatively large spatial extent or for transitions with a high spectral density of oscillator strength. Compensating effects, however, appear to mitigate the effect of condensation for both hexafluorbenzene and tetramethylsilane.

Introduction

In preparation for a study of the photoionization efficiencies of some simple liquid mixtures, we discovered that there were essentially no data available in the literature on liquid absorption spectra in the needed VUV region of the spectrum. The present study was initiated, in part, to repair this deficiency. Additionally, however, since the effects of condensation on the spectroscopy of higher excited states of molecular systems has considerable interest in its own right, some features of these effects are also considered here.

The molecules that we have chosen have all been earlier studied in the gas phase. As we will demonstrate below, the effect of condensation is not easily predictable. In a previous study of the allowed $S_0 \rightarrow S_3$ transition (hereafter referred to as $N \rightarrow V$) in benzene liquid at ca. 185 nm,[1] it was shown how severely the absorption maximum is red-shifted and the oscillator strength redistributed compared to the vapor. We continue to see this effect for toluene, but for hexafluorobenzene a much weaker redistribution is observed. For tetramethylsilane, whose vapor spectrum appears to be dominated by Rydberg transitions,[2,3] we find essentially no change in either the positions of its absorption bands nor in the spectral distribution of its oscillator strength up to 120 nm. On the other hand, for the saturated hydrocarbons (where also many of the excited states have been assigned as Rydberg-like),[2,3] we see, in addition to some slight blue shifting of the lower lying transitions, an unexpectedly strong decline in total oscillator strength to 120 nm. The origins of all of these effects are briefly considered.

Experimental Section

As has been described earlier,[1] our absorption cell consists of two 2.54 cm diameter and 0.1 cm thick polished MgF_2 windows clamped together and sealed via indium wire. The cell could be evacuated to 1×10^{-5} Torr. All liquids were degassed by repeated freeze–pump–thaw cycles and then vacuum distilled into the cell. A nitrogen-flushed Cary 15 spectrophotometer was used for measurements from 300 to 170 nm.

For measurements down to 120 nm, light from a Hamamatsu L879 D_2 lamp (fitted with MgF_2 window) was spectrally dispersed by a nitrogen-flushed Acton VM502 (0.2 m) mono-

chromator (operating at 1 nm band-pass), transmitted through the cell, and focused via a parabolic mirror onto the surface of a quantum counter (microcrocrystalline 2,5 -diphenyloxazole, PPO, deposited on a quartz surface). The front surface emission from the PPO was collected by a Suprasil quartz lens and focused onto the entrance slit of a McPherson 218 (0.3 m) monochromator to which was affixed on the exit slit a thermoelectrically cooled photomultiplier (Hamamatsu R943-02). The intensity of the light was measured by photon counting and the experiment controlled by an IBM PC computer via a Data Translation DT2801 board. Stray light contributions were determined both by (a) insertion into the excitation path of a Suprasil quartz flat and (b) replacing the N_2 flush with air. Both sets of measurements agreed from 120 nm to the quartz cutoff at 157 nm. The cell path lengths were obtained by calibration with the well-known benzene spectrum[1,4,5] either inserted in the cell as a pure liquid or added as a low concentration impurity to the liquid being studied.

2,2,4-Trimethylpentane (Aldrich, 99% photometric grade), 2,2-dimethylbutane (Aldrich, 99%), *n*-pentane (OmniSolv, glass distilled), and tetramethylsilane (Aldrich, NMR grade 99.9%) were all further purified by percolations through 1 m long columns of activated silica gel. Both benzene and toluene (Fisher Spectroanalyzed) were first distilled under vacuum and then stirred with activated 4A molecular sieve and stored under nitrogen. Hexafluorobenzene (Aldrich, 99.9%) was used without further purification. All measurements were made at 21 ± 1° C.

Results and Discussion

A. Benzene and Toluene. The absorption spectra of neat liquid benzene and toluene are shown in Figure 1 and compared with vapor spectra reported by Bolovinos et al.,[6] Pantos et al.,[7] and Koch and Otto.[8] Comparison of the toluene vapor[7] and liquid spectra shows that in the wavelength region of the stongly allowed $N \rightarrow V$ transition at ca. 178 nm in benzene and 200 nm in toluene, there are similar shifts and redistribution of oscillator strength, as has been previously reported for benzene.[1,4] In regions where the absorption becomes relatively weak (i.e., from 120 to 160 nm and for $\lambda > 200-205$ nm),[7,8] there is much less of an influence of condensation. The spectral region, $\lambda > 200$ nm has been commented on previously.[1] For $\lambda < 170$ nm, our results for liquid benzene are in good agreement with

* Corresponding author. E-mail: lipsky@chem.umn.edu. Fax: 612-626-7541.
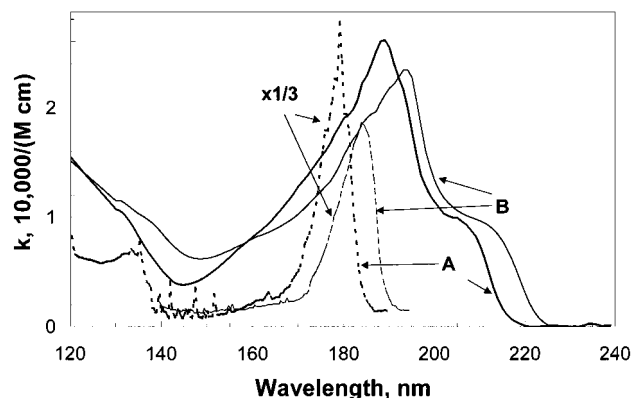
Figure 1. Absorption spectrum of benzene (A) and toluene (B). Solid lines are the liquid spectra and dashed lines are vapor spectra taken from Bolovinos et al.[6] for benzene and toluene above 140 nm and from Pantos et al.[7] and Koch and Otto[8] for benzene from 140 to 120 nm.

TABLE 1: Experimental Oscillator Strengths, f_{exp}, Calculated over Indicated Ranges of the Absorption Spectrum of Various Liquids

substances	range of energies, eV	f_{exp}[a]
benzene	5.50−6.06	0.081
	6.08−8.52	1.0
	8.58−10.3	0.34
toluene	5.00−5.97	0.11
	5.99−8.35	1.0
	8.40−10.3	0.49
hexafluorobenzene	5.99−6.47	0.081
	6.54−8.95	1.0
	9.02−10.3	0.20
tetramethylsilane	6.50−7.97	0.21
	7.97−9.50	0.53
	9.50−10.3	0.47
2,2-dimethylbutane	6.86−10.3	0.79
2,2,4-trimethylpentane	6.86−10.3	0.80

[a] $f_{exp} = m_e(2\pi^2\alpha\,\hbar)^{-1}\int\sigma\,d\omega$, where α is the fine structure constant, $\sigma = 2303k/L$, k is the decadic absorptivity, L is Avogadro's number, and $\hbar\omega$ is the transition energy. The integrations simply begin and end at the lower and upper ends of the integrated ranges.

those of Inagaki.[5] In the liquid, there is observed a minimum in absorptivity, k, at ca. 145 nm (148 nm in toluene) followed by a rapid rise of k from 145 to 120 nm by a factor of ca. 3.7 (3.1 in toluene). In the vapor phases,[6−8] the positions of the minima and the ratios of k at 120 nm to that at the minima are essentially the same.

The importance of a large spectral density of oscillator strength ($df/d\omega$) in influencing the benzene liquid spectrum has been previously commented on[1] and is not considered further here. The relatively smaller effect of condensation on the N → V transition in toluene is consistent with these views. Thus, the peak absorptivity in the vapor spectrum of toluene[6] is ca. 20% lower than for benzene with a full width at half-height that is ca. 40% larger. In the liquid, the absorptivities and widths are about the same for both substances. Table 1 lists the experimental oscillator strengths for various regions of these spectra.

B. Hexafluorobenzene. In Figure 2, we present the liquid absorption spectrum of hexafluorobenzene together with a vapor spectrum (from 130 to 280 nm) reported by Philis et al.[9] In this region, Philis et al.[9] identify four major transitions with peaks (and assignments) at 231 nm (as $\pi \rightarrow \sigma^*$), 194 nm ($\pi \rightarrow \pi^*$), 174 nm ($\pi \rightarrow \pi^*$), and 161 nm ($\sigma \rightarrow \pi^*$). The intense transition at 174 nm is of the same nature as the N → V transitions in benzene and toluene.
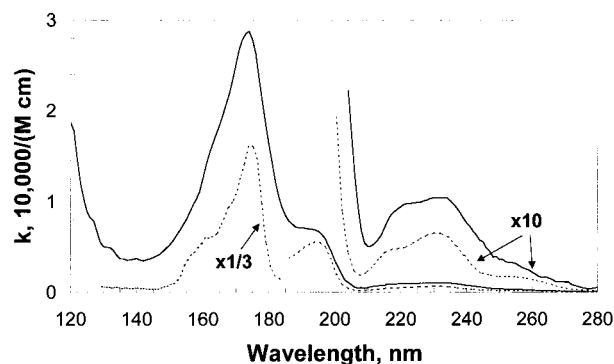
Figure 2. Absorption spectrum of hexafluorobenzene. The solid line is the liquid spectrum and the dashed line is the vapor spectrum taken from Phillis et al.[9]
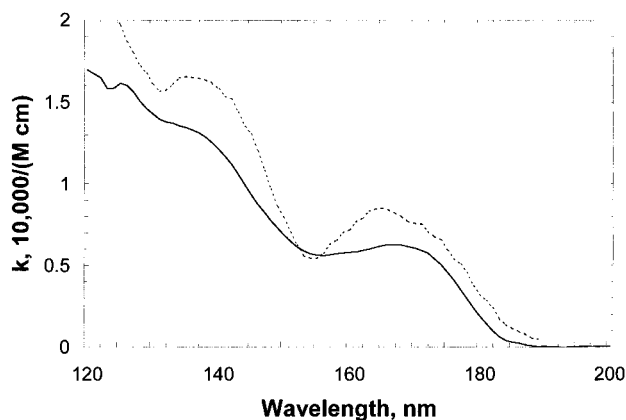
In the neat liquid of hexafluorobenzene, the same four transitions are observed at positions only very slightly displaced from the vapor, i.e., at 232, 192, 174, and 162 nm, respectively. The absorptivitiy of the N → V transition at 174 nm is reduced in the liquid vis-à-vis the vapor, but much less so than is the case for the corresponding transitions in benzene and toluene. The reported[9] oscillator strength for this transition in the vapor of 0.9 and also for the weaker $\pi \rightarrow \pi^*$ transition at 194 nm of 0.085 agree well with the liquid values displayed in Table 1. Indeed, the major effect of condensation here seems to be simply a broadening of the vapor N→V transition without the concomitant strong red shift observed for the related transition in the case of benzene (i.e., 0.41 eV from ca. 178.2 to 189.5 nm).[1,4] Since the oscillator strength is essentially unaffected by condensation, the broadening in hexafluorobenzene is manifested by a reduction in the absorptivity at 174 nm by a factor of ca. 1.7 and some small increases in absorptivity of the lower transitions (due to more extensive overlapping with the 174 nm transition).

Although not shown in Figure 2, we have also examined a dilute solution spectrum of hexafluorobenzene in n-pentane over the spectral region from 300 nm up to the n-pentane cutoff at ca. 170 nm. The lower transitions at 231 and 194 nm are at the same positions as the vapor spectrum and with very similar absorptivities at their maxima (within ca. 20%). However, the N → V transition in n-pentane is shifted to the red of its position in the liquid by 0.14 eV to 177.5 nm (albeit with an absorptivity within ca. 3% of its vapor value). Accordingly, unlike benzene, for which this transition is *red*-shifted by ca. 0.19 eV in passing from a dilute solution to neat liquid,[1] in the case of hexafluorobenzene, there is now a *blue shift*.

The blue shift is not unexpected. As has been documented for many systems, molecular electronic transitions tend to exhibit relatively minor differences from their vapor phase behavior (both in their spectroscopy and in their photophysical properties) when imbedded in perfluorcarbon environments.[10]

It is this electronic inertness of the fluorine environment, we suggest, that also acts to thwart the expected red shift of the N → V transition in passing from vapor to liquid C_6F_6.

C. Tetramethylsilane. Our VUV spectrum of liquid tetramethylsilane is presented in Figure 3 together with a vapor spectrum reported by Roberge et al..[11] Recent density functional theory (DFT) calculations,[12] confirm previous views[2,3,11] that Rydberg transitions dominate the electronic spectrum in the region displayed in Figure 3 and that valence transitions develop only to the blue of ca. 125 nm. The first absorption band, an allowed N → 4s Rydberg transition,[2,3,11−15] onsets at about 189 nm, has its maximum at 166 nm ($k = 7.5 \times 10^3$ M^{-1} cm^{-1})

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Figure 3. Absorption spectrum of tetramethylsilane. The solid line is the liquid spectrum and the dashed line is the vapor spectrum taken from Roberge et al.[11]

and declines to a minimum at 155 nm ($k = 5 \times 10^3$ M^{-1} cm^{-1}). The N $\rightarrow$ 4p Rydberg transition is symmetry forbidden in the vapor and considered responsible for the minimum in absorptivity at 155 nm.[2,3,11] At shorter wavelengths there appears the relatively strong N $\rightarrow$ 3d Rydberg transition[2,3,15] that maximizes at 135 nm with $k = 1.6 \times 10^4$ M^{-1} cm^{-1}.

As is clear from Figure 3, condensation leaves all of these features relatively unaffected except for a somewhat higher energy onset of the N $\rightarrow$ 4s transition, a slight red shift in its maximum, and some overall general broadening of the spectrum. Table 1 lists the experimental oscillator strengths for various regions of the liquid spectrum. This insensitivity of the spectrum is particularly noteworthy in view of the DFT calculations,[12] which predict expectation values of r^2 for the 4s, 4p, and 3d Rydberg states to extend beyond the value of $\langle r^2 \rangle$ for the ground state (26 A^2) by ca. 14, 23, and 42 A^2, respectively. Such relatively large spatial extents of the terminal state of the absorptions might have been expected to lead to a more extensive shifting of the spectrum on condensation.[2,3,16−18] An underlying layer of valence transitions[2,3] in the 120−200 nm region could also accommodate the observed insensitivity, since the valence states would normally be expected to be only slightly perturbed, but it is difficult to reconcile such a conjecture with the success of the DFT calculations[12] in predicting both spectral positions and much of the oscillator strength distribution.

Broadening and shifting of Rydberg states by foreign gas perturbers has been the subject of numerous theoretical studies.[17−20] In general, these have been confined to high Rydberg states perturbed at sufficiently low pressures that the impact limit of line broadening theories has been applicable. An impulse approximation, first implicitly employed by Fermi[21] and subsequently refined by others[22,23] permits the perturbation for high Rydberg states by neutral perturbers to be separately calculated for the positive core and for the pseudo free electron. Perturbation of the core gives always a negative shift to the spectral line proportional to the polarizability of the perturber whereas the shift due to the electron is related to its scattering length in the field of the perturber and, accordingly, can be negative or positive depending upon the characteristics of the pertuber-electron potential. In general, the theory has been rather successful in predicating broadening and shifts as a function of principal quantum number down to $n \approx 5$ and particle density up to ca. 10^{15} cm^{-3}.[17−20,24]

At the densities of the room-temperature liquids studied here of ca. 5×10^{21} cm^{-3}, the so-called statistical rather than impact limit of broadening theories is expected to apply.[25] But,

still, for states of large n ($n > 5$, at least where these states can be identified, as for example for simple molecules in rare gas matrixes),[26,27] the separation of the perturbation calculation into its core and Rydberg electron parts appears to remain a satisfactory approximation with predictions of spectral shifts proportional to solvent polaraziblity and scattering length, respectively.[26,28]

For Rydberg states of lower principal quantum number the theoretical situation is much more complex.[29−31] Experimentally, it is generally observed that unlike valence transitions, which are slightly red-shifted in *n*-alkane solvents, the shift of the lowest molecular Rydberg state is usually to the blue,[2,3] and, indeed, this difference is sometimes used as a criterion to distinguish the two types of transition.[2,3,28,32] However, in the solvent tetramethylsilane, it has been observed that the blue-shifting effect is much reduced[33] and, indeed, for benzene as solute, the N $\rightarrow$ 3s transition appears to even red shift with respect to its position in the vapor.[34]

The spectral line shift of low-lying Rydberg transitions has a blue contribution that is ultimately a consequence of repulsive interactions between the Rydberg electron and the solvent.[29−31] A red-shifting contribution comes from solvent polarization induced by the charge distribution of the excited state. This is dependent on both the polarizability of the solvent and how spatially diffuse is the excited state. Since the differences in solvent polarizability (at least as manifested by the refractive index) are not sufficiently disparate to explain the different spectral shifts in *n*-alkanes and tetramethylsilane, the differences instead are considered to derive from the effect of the solvent to alter the spatial diffuseness of the excited state.[33,34] The more diffuse is this state, the more independently can solvent polarization develop about the positive core and about the electron.

Liquids such as tetramethylsilane that are composed of approximately spherical molecules which, individually, have negative scattering lengths are usually observed to have large vertical electron affinities ($-V_0$), to support excess thermal electrons with high mobility (μ), and to have anomalously low thresholds for photoioniziation of dissolved solutes.[35,36] The negative V_0 and high mobility for the excess electron imply a tendency for it to delocalize and, for a low-energy Rydberg electron, suggest description by a wave function more diffuse than would be expected in more inert solvents. Also, the large lowering of the photoionization threshold points to relatively small electron kinetic energies of excited states in liquid tetramethylsilane.

As pointed out above, negative contributions to the spectral shift will derive from these effects and from our results in Figure 3 appear to be sufficiently large to mitigate the usual observed blue shifting on condensation. The reduced absorption coefficient of the liquid relative to the vapor may also have its origins in the increased diffuseness of the excited state. Indeed, this has been suggested to explain a similar reduction in the absorption coefficient of low Rydberg states of certain organic amines in liquid tetramethylsilane vis-à-vis the *n*-alkane solvents.[33] Unfortunately, there is no available theory to quantitatively describe these solvent effects on the spatial extent of the Rydberg electron and its consequences to line broadening and shifts.

D. 2,2-Dimethylbutane and 2,2,4-Trimethylpentane. The vapor phase spectra of a number of saturated hydrocarbons have been previously reported by Lombos, et al.[37] and by Raymonda and Simpson.[38] In the spectral range 175−120 nm, the dominant transitions have been suggested to be to states of predominantly
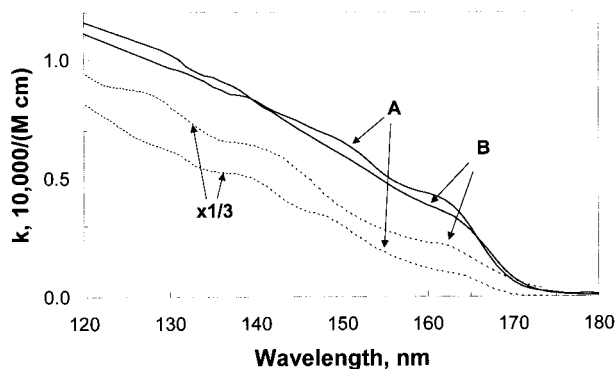
Figure 4. Absorption spectrum of 2,2-dimethylbutane (A) and 2,2,4-trimethylpentane (B). Solid lines are liquid spectra, and dashed lines are vapor spectra taken from Raymonda and Simpson[38]

$n = 3$ Rydberg character.[2,3] Recent Xα−SW calculations and analysis of NEXAFS spectra of a number of *n*-alkanes support this view.[39,40]

In Figure 4 we reproduce the vapor spectra reported by Raymonda and Simpson[38] for 2,2-dimethylbutane (A) and 2,2,4-trimethylpentane (B) for comparison with our neat liquid spectra. For both substances, there appear to be very broad structures in their spectra in both phases, but we have been unable to unequivocally decide which structures are correlated in the two phases. The most striking difference between the liquid and the vapor is the surprisingly large disparity in absorption coefficients. For wavelengths below 160 nm the vapor spectrum is ca. 2× more intense than the liquid. An apparent loss of oscillator strength in the liquid is consistent with the view that the absorptivity in this region becomes blue-shifted to energies above 120 nm but the magnitude of this effect remains surprising. It should be noted that both liquids have V_0 values that are only ca. 30−40% that of tetramethylsilane (V_0(TMS) = −0.62 eV) and support thermalized electrons with mobilities reduced by more than 1 order magnitude (μ(TMS) = 100 cm^2 V^{-1} s^{-1}).[35,36]

Conclusions

We have compared the liquid phase spectra of benzene, toluene, hexafluorbenzene, tetramethylsilane, 2,2-dimethyl-butane, and 2,2,4-trimethylpentane with previously reported vapor phase spectra. For benzene and toluene our results are consistent with previous suggestions concerning the influence of the spectral density of oscillator strength on the effect of condensation. For hexafluorobenzene, vapor and neat liquid spectra were found to be much more similar than for benzene and toluene and attributed, at least in part, to the well-known weakness of a perfluorocarbon environment in perturbing spectroscopic properties. For tetramethylsilane, all of whose vapor transitions to 120 nm have been assigned as transitions to low lying Rydberg states, we find essentially no changes in spectrum nor absorptivities from 200 to 120 nm. It is suggested that the absence of the usually expected blue shift caused by repulsive perturbations on the Rydberg electron is canceled in this case by the red-shifting consequences associated with the large vertical electron affinity and high mobility of excess electrons in this solvent. For liquid 2,2-dimethylbutane and 2,2,4-trimethylpentane, blue shifting of the transitions to 3p and 3d Rydberg states is suggested to be the origin of a large observed loss of oscillator in the spectral region 150−120 nm.

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