

Spectroscopic Evidence for Long-Range Repulsive Intermolecular Forces*

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Experimental results are presented on the shift of wavelength of absorption of benzene, naphthalene, pyrene, and phenanthrene with density of the diluents helium and nitrogen. Arguments are presented to show that the blue shift observed in the benzene ^1L_b spectrum in helium is neither due to short-range repulsive forces nor to long-range dispersive forces. It is presumed that there are weak, long-range, non-dispersive forces present in the benzene-helium interaction that have the character of repulsive forces.

INTRODUCTION

THE effects of a nonpolar diluent on the electronic energy levels of a nonpolar light absorber are generally understood in terms of London dispersion forces. Since the interaction between light absorber and diluent is usually greater for the absorber in an excited than in the ground electronic state, spectral shifts are usually to the red.¹ Short-range repulsive forces, characterized by the higher exponential term in a Lennard-Jones 6-12 type potential, do not usually have to be considered in interpreting molecular spectral shifts.

In an apparently anomalous behavior, the vapor absorption spectrum of benzene in the near ultraviolet was found to shift to the blue in the diluent helium.²⁻⁴ The shift was approximately linear with density and the bands remained very sharp from low to high diluent densities. These results along with the low polarizability of helium suggested that the blue shift was a result of the predominance of repulsive over attractive forces. However, the linear shift and the sharpness of the bands were difficult to reconcile with short-range repulsive forces. It seemed probable that the long-range dispersive interaction was simply less for the absorber in the excited state than in the ground state in this particular case. This report is the result of attempts to clarify the nature of the interactions producing the blue shift.

EXPERIMENTAL AND RESULTS

The spectroscopic equipment and techniques have been described.⁵ The pressure system used in solution work⁶ has been modified only by the addition of a 10-cm absorption cell and a heating coil usable up to 200°C. The condensed ring aromatic hydrocarbons used were

those with a sufficient vapor density in helium at temperatures within the 200° range to give a satisfactory absorption spectrum in a 10-cm path. Benzene, naphthalene, phenanthrene, and pyrene satisfied these conditions. With the sample in a small boat at the bottom of the pressure cell, the temperature of the cell was raised until the desired transition was of the proper density. Upon increasing the helium density, the vapor density of the sample remained approximately constant, apparently decreasing slightly for benzene and naphthalene and increasing slightly for the other aromatics. This was in marked contrast to the solubility in nitrogen, which increased rapidly with increasing nitrogen density for all the compounds. A range of shorter absorption path lengths used with nitrogen made it possible to cover, stepwise, a reasonable nitrogen density range at a given temperature. The results are presented in Fig. 1 and in Table I.

The effects of an increase in temperature on the wavelength of absorption at a given diluent density were observed separately. For benzene in helium at 1000 psi pressure, where the benzene bands were still sharp, a change in temperature from 20° to 200° caused a wavelength shift of the 2589 Å band of less than 0.1 Å. Likewise, no temperature induced wavelength shifts were observed in the spectra of the other aromatics. This agrees with the observations of Robin⁷ on phenanthrene in various gaseous diluents and is not inconsistent with the results of Sambursky *et al.*⁸ where the benzene vapor was examined at temperatures up to 287°C and at the corresponding pressures of the saturated vapor.

The densities of helium⁹ and nitrogen¹⁰ over suitable temperature ranges and at pressures up to 1000 atmos were available.

DISCUSSION

The usual forms of the intermolecular potential curves presented in Fig. 2 show the effect of long-range dispersion forces and short-range repulsive forces on the

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¹ H. Margenau and W. W. Watson, *Revs. Modern Phys.* **8**, 22 (1936).

² B. Oksengorn, Symposium on the Optical and Acoustical Properties of Compressed Fluids, National Center of Scientific Research, Bellevue, France (1957).

³ Robertson, Babb, and Weigang, reference 2.

⁴ Babb, Robinson, and Robertson, *J. Chem. Phys.* **30**, 427 (1959).

⁵ Robertson, Weigang, and Matsen, *J. Mol. Spectroscopy* **1**, 1 (1957).

⁶ D. S. Hughes and W. W. Robertson, *J. Opt. Soc. Am.* **7**, 577 (1956).

⁷ Stephane Robin, *Compt. rend.* **230**, 1757 (1950).

⁸ Sambursky, Halperin, and Heinig, *J. Chem. Phys.* **21**, 2041 (1953).

⁹ Wiebe, Gaddy, and Heins, *J. Am. Chem. Soc.* **53**, 1721 (1931).

¹⁰ Bartlett, Cupples, and Tremarne, *J. Am. Chem. Soc.* **50**, 1275 (1928).

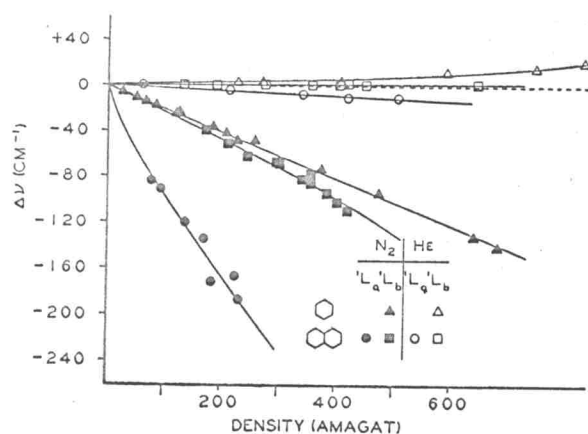


Fig. 1. Frequency shifts of the ^1L_b band of benzene and the ^1L_b and ^1L_a bands of naphthalene with relative density of the diluents helium and nitrogen.

ground and excited state energy levels (E_o and E_i) of a light absorber a distance R from a perturber. Transitions occurring at relatively large intermolecular separations, for example at R_2 , would be expected to show a red shift and those at very close separations such as R_3 a blue shift with respect to absorption by the isolated molecule. The total effect of a diluent on a light absorber would be expressed by the sum of the pairwise interactions over the total molecular environment. If V_i and V_o are the interaction potentials, N the mean number density of perturbers and $g(R)$ a distribution function and if the potentials are directly additive, then the total frequency shift may be expressed as

$$\Delta\nu_{oi} = (4\pi N/hc) \int g(R) [V_i(R) - V_o(R)] R^2 dR. \quad (1)$$

If a Lennard-Jones 6-12 type potential is now assumed to represent both the excited and the ground state potentials, that is $v_i \sim a_i R^{-12} - b_i R^{-6}$ and $v_o \sim a_o R^{-12} - b_o R^{-6}$, then $v_i(R) - v_o(R)$ in Eq. (1) is proportional to $aR^{-12} - bR^{-6}$, where $a = a_i - a_o$ and $b = b_i - b_o$. Taking the mean number density N to be proportional to the diluent density ρ , Eq. (1) may be rewritten as

$$\Delta\nu_{oi} = (\text{const}) \rho \left[\int g(R) a R^{-10} dR - \int g(R) b R^{-4} dR \right]. \quad (2)$$

The red shift usually observed with increasing solvent or diluent density is attributable to the predominance of the second term above and to the positive value of the constant b . Similarly, a blue shift could indicate either the predominance of the first term or a negative value of b . The smallness of the shifts observed attests to the smallness of the constants a and b .

Michels and De Kluiver¹¹ observed a blue shift of the 2536-A mercury line in helium that was linear to densities of about 110 amagat and then increased more

rapidly with increasing density. They expressed the net interaction potential as above and attributed the low-density, linear blue shift to a negative value of the constant b , that is, the dispersion forces were assumed to be larger for the light absorber in the ground than in the excited state. The rapidly increasing blue shift at higher densities was attributed to the predominance of short-range repulsive forces.

With benzene in helium, the blue shift is approximately linear to extreme densities of around 1100 amagat and then increases more rapidly to the density limit of the experiment at 1600 amagat.⁴ If the distribution function $g(R)$ is at least approximately constant with increasing density in Eq. (2), the integrals are constant and the frequency shift is proportional to the density of the diluent. Experimental results indicate that this is a good approximation over an extreme density range. Thus, whatever mechanism accounts for the blue shift at low helium densities is still operative at densities of 1100 amagat. It will first be shown below that the low-density blue shift of benzene in helium could not be attributed to short-range repulsive forces, from which it follows that the shift at high densities (to 1100 amagat) is also not attributable to such forces. It will then be shown that the sign of b in the potential term is not negative, as is assumed by Michels and De Kluiver for the mercury-helium system. The conclusion then follows that there are forces present other than the short-range repulsive forces or the long-range dispersion forces.

In molecular electronic spectra, where the electronic transition time is small in comparison to the period of molecular vibrations, i.e., $\ll 10^{-13}$ sec. if the Franck-Condon principle applies, perturbing atoms may be always considered as at rest during electronic transitions. The concepts of classical collision damping theory applicable to atomic spectra at relatively low gaseous densities have no meaning for molecular spectra. On the other hand, statistical theories that apply to atomic spectra at high diluent densities should apply to molecular spectra at all densities. Statistically, the position of the center of a displaced band should represent the combined effect of the majority of the effective perturbers. At low diluent densities where the time between close encounters is large in comparison to the time spent

TABLE I.

Compound	Transition	f Value	Frequency (cm^{-1})	Frequency shift ($\text{cm}^{-1}/\text{amagat}$)	
				N_2	He
Benzene	^1L_b	0.002	38 620	0.20	-0.018
Naphthalene	^1L_a	0.18	37 330	0.70	0.020
Naphthalene	^1L_b	0.002	32 460	0.25	-0.003
Phenanthrene	^1L_a	0.18	35 260	0.90	0.03
Phenanthrene	^1L_i	0.003	29 160	0.11	~ 0.03
Pyrene	^1B_b	0.47	37 750	0.83	0.037
Pyrene	^1L_a	0.47	31 050	0.88	0.043

¹¹ A. Michels and H. De Kluiver, *Physica* **22**, 919 (1956).

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in close encounter, the position of the center of the band could only correspond to rather distant or "optical" collisions. The shapes of the edges of absorption bands are usually considered to reflect interactions occurring close to the absorber where the energy levels are more strongly perturbed.

Thus the linear blue shift of the benzene spectrum from the very lowest helium densities, together with the sharpness of the bands to very high densities, are considered conclusive indications of the predominance of long-range interactions.

The relatively slight importance of repulsive forces in optical phenomena is also exemplified by the shift of the benzene spectrum in the diluents nitrogen and argon, although here the dispersion forces are considerably larger than in helium. At diluent densities as high as 700 amagat no effect attributable to repulsive forces was noticeable in the benzene spectrum in nitrogen,⁴ the red shift being approximately linear from the lowest nitrogen density on up. In the slightly less polarizable argon diluent, a decreasing red shift at the higher densities indicated the increasing importance of repulsive forces. However, in the same high-density range Zwanzig¹² was able to treat the equations of state of both nitrogen and argon by considering the dispersion forces as perturbations on repulsive forces. Thus, even under conditions where the short-range repulsive forces play the major role in determining equilibrium properties of gases, their effect on absorption spectra is still small.

The effect of temperature on the broadening and shift of atomic resonance lines in gaseous diluents has been observed by Hull,¹³ among others, and the results were consistent with the theory developed by Margenau. At low densities of perturbers an increase in "velocity" broadening with increasing temperature was observed. At relative diluent densities above 8 or 9 "statistical" broadening predominated and was insensitive to temperature. As pointed out in the foregoing, only statistical considerations have meaning in molecular spectra and if only inverse 6th power attractive potentials are assumed, as by Margenau, then no temperature effect should appear here. However, if the blue shift is attributed to short-range repulsive forces, the more penetrating collisions at higher temperatures should enhance the shift. Since no such increase was observed, the short-range forces must not be a determining factor. The fact that high temperature gaseous diffusion can be interpreted by considering only repulsive potentials¹⁴ illustrates again the relatively long-range nature of optical interactions.

The nature of the London-Van der Waals forces is well understood and is successfully used to interpret

the gross features of spectral shifts in complex systems. For example, the red shift of the benzene spectrum in a number of diluent gases was found to vary roughly with the calculated ground-state dispersion energy.⁴ In another set of experiments, the red shift for a number of electronic transitions of condensed-ring aromatics in pressurized solution was found to increase with the oscillator strength of the transition, again in qualitative agreement with dispersion theory.⁵ Hence the essential correctness of the London dispersion equation in representing the long-range attractive forces between two nonpolar molecules is accepted, and its application to complex systems is experimentally justified. As expressed by Margenau and Watson,¹ the frequency shift is given by

$$\Delta\nu_{oi} = (\text{const})\rho \left[\sum_k' \frac{f_{ok^A} f_{ok^B}}{E_k^A E_k^B (E_k^A + E_k^B)} - \sum_{k \neq i} \frac{f_{ik^A} f_{ok^B}}{(E_k^A - E_i^A) E_k^B (E_k^A - E_i^A + E_k^B)} \right], \quad (3)$$

where $E_k^A(E_k^B)$ is the energy of the k th state of the absorber (diluent) relative to its ground state, and $f_{ok^A}(f_{ok^B})$ is the oscillator strength of the $o \leftarrow k$ th transition of the absorber (diluent). The assumed constancy of the integral over R has been included in the foregoing expression. The experimental results to be compared are the strong red shift of the benzene spectrum in argon and its weak blue shift in helium. For the sake of this comparison it is convenient to replace the energy levels E_k^B of the diluent by a mean value, which is approximately its ionization energy I_B . Also, the oscillator strength of the diluent may be replaced by its approximate expression in terms of the polarizability of the diluent, as in Margenau and Watson. These are good approximations for the diluents helium and argon. The expression for the frequency shift is then

$$\Delta\nu_{oi} = (\text{const})\rho I_B \alpha_B \left[\sum_k' \frac{f_{ok^A}}{(I_B + E_k^A) E_k^A} - \sum_{k \neq i} \frac{f_{ik^A}}{(I_B + E_k^A - E_i^A) (E_k^A - E_i^A)} \right]. \quad (4)$$

The change from a red shift in argon to a blue shift in helium would correspond to a change from the predominance of the second series of terms above to that of the first. The change from I_B (argon) = 17.5 eV to I_B (helium) = 24.5 eV decreases the magnitude of the negative terms with respect to the positive terms by a few percent. However, if the polarizability of benzene in the excited state is at least as large as that in the ground state, the sum of the negative terms still seems to be more than twice that of the positive terms. This qualitative conclusion is arrived at in the following manner. Assume that E_k^A for benzene can be replaced by I_A , the ionization energy of benzene, and that

¹² J. Zwanzig, J. Chem. Phys. 22, 1420 (1954).

¹³ G. F. Hull, Jr., Phys. Rev. 51, 572 (1937).

¹⁴ R. E. Walker and A. A. Westenberg, J. Chem. Phys. 29, 1147 (1958).

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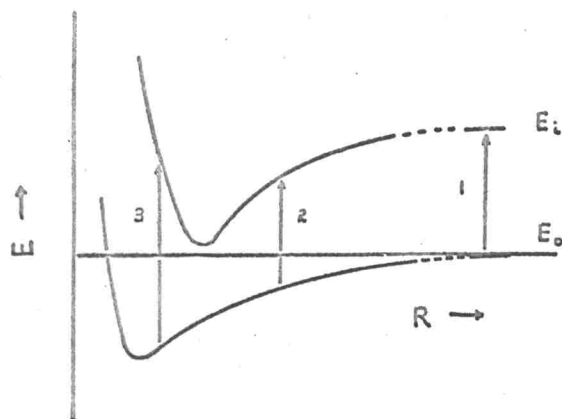


Fig. 2. Ground and excited state intermolecular potentials in terms of which spectral shifts are usually understood.

$E_k^A - E_i^A$ can be replaced by $I_A/2$. Here $I_A = 9$ ev and $E_{iA} = 4.7$ ev. The ground state polarizability α_A is substituted for $\sum_k f_{ok}/I_A^2$ and the excited state polarizability α_A^1 for $\sum_k f_{ik}/I_A^2$. The terms in the brackets in Eq. (4) can then be expressed as

$$\{\alpha_A[I_A + I_B]^{-1} - 4\alpha_A^1[I_A + 2I_B]^{-1}\},$$

and the negative term, not considering the polarizability, is 2.4 times the positive terms for helium. Also the assumptions made would tend to decrease the negative terms more than the positive. If the foregoing argument is not so nebulous as to have lost all meaning, then the exchange of helium for argon in Eq. (4) could not result in a change in the sign of $\Delta\nu$. Thus, if the dispersion forces tend to produce a red shift when argon is the diluent, they must also tend to produce a red shift with helium. The explanation of the low-density blue shift in helium in terms of a negative value of the constant b in Eq. (2), as by Michels and De Kluiver for mercury in helium, evidently cannot be applied here.

The results presented in Fig. 1 and Table I support the conclusion that the dispersion forces for the excited state benzene interaction with helium are greater than

for the ground state and so contributes to a red shift. If the blue shift were due to dispersion forces, then increasing the dispersion forces would result in an increased blue shift. The experimental results are that in the systems similar to benzene, the naphthalene, phenanthrene and pyrene, the higher oscillator strengths show a progressive red shift in helium. In the more polarizable nitrogen diluent, the shifts are all to the red and proportionately larger than in helium. If the total effect of the diluent on the light absorber is considered to be a long-range repulsive force and a long-range attractive force, each larger for the excited state benzene than for the ground state, and if the repulsive forces are relatively independent of the polarizability of the light absorber or diluent while the attractive forces behave according to dispersion theory, then the results of Table I are understandable.

It is therefore suggested as a possibility that there are weak long-range repulsive forces in the benzene-helium interaction and that they are noticeable only as a result of the low polarizability of the helium diluent and the low oscillator strength of the ^1L_b transition of benzene. In this case the spectral effects should provide sensitive indications of the presence of such forces.

The only theoretical evidence in substantiation of relatively long-range repulsive forces seems to be in the calculation of the interaction of a normal helium atom with either a singlet or triplet metastable helium atom by Buckingham and Dalgarno.¹⁵

It should be pointed out that the foregoing discussion considers the shift of the center of intensity $\bar{\nu}$ of the line and not its maximum, ν_{max} , which was actually measured. However, it is practically impossible to deal adequately with the difference between the two in these complex systems.[†]

¹⁵ R. A. Buckingham and A. Dalgarno, Proc. Roy. Soc. (London) A213, 327 (1952).

[†] For a consideration of the effects of pressure on electronic band shapes of aromatic molecules, see O. E. Weigang, Jr., and W. W. Robertson, J. Chem. Phys. 30, 1413 (1959).

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¹ G. E. K.
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² E. Bergm
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³ N. J. Leon
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⁴ H. H. Jaff