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Submitted to: Chemical Physics Letters

UCRL-18130
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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FREQUENCY SHIFT OF THE STRETCHING VIBRATION OF I_2 IN LIQUID MIXTURES

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The optical properties of various iodine solutions have been investigated by many authors.[1] Benesi and Hildebrand[2] first observed a new absorption band in the ultraviolet spectra of solutions of iodine in aromatic hydrocarbons. This absorption band has been attributed by Mulliken[3] to the formation of charge-transfer complexes between iodine and hydrocarbon molecules. Infrared absorption by iodine in pyridine complexes and in benzene has also been studied by Plyler and Mulliken.[4] The iodine fundamental vibration in these solutions shows a frequency shift from its vapor value which is also attributed to the formation of charge-transfer complexes. In principle, Raman spectroscopy would be more suitable for the investigation of the iodine vibration; however, as far as we know, no detailed Raman spectrum of iodine has ever been reported. Using a He-Ne laser as the exciting source, we have now obtained the Raman spectra of iodine in various solutions. In particular, we have measured the frequency shifts of the iodine fundamental vibration in liquid mixtures of benzene (or methylated benzenes) and some inert solvent, such as n-hexane, as a function of the benzene (or methylated benzene) concentration. Our results cannot be explained satisfactorily by the simple model of Orgel and Mulliken on charge-transfer complexes.[3] Nevertheless,

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by generalizing their model using interaction potential between molecules, we have succeeded in interpreting our experimental findings.

The construction of our Raman spectrometer was the same as that of Porto.[5] The stretching vibration of iodine in the vapor phase has a characteristic frequency of 213 cm^{-1}.[6] For iodine in n-hexane, we observed that the vibrational spectral line was shifted to 210 cm^{-1}. When benzene was added into the solution, the line gradually shifted to an even lower frequency with no appreciable broadening. The frequency shift was more pronounced if methylated benzene instead of benzene was used. With mesitylene at low concentrations, however, the spectral line showed two distinct peaks, one at 210 cm^{-1} and the other at 202.5 cm^{-1}. As the mesitylene concentration was increased, the peaks remained unshifted, but the relative intensity of the peaks changed; the 210 cm^{-1} peak diminished and the 202.5 cm^{-1} peak grew. Finally, at sufficiently high concentration, the weak peak disappeared and the strong peak started to shift to lower frequencies. In Fig. 1, for a reason to be seen later, we have plotted the frequency shift of the center of gravity of the I_2 vibrational spectrum as a function of the concentration of benzene or methylated benzene in n-hexane. Similar results were also obtained for iodine in other inert solutions, such as CCl_4 and n-heptane.[7] Note that the dielectric constants of CCl_4 and benzene are approximately the same.

The frequency shift with benzene or methylated benzene concentration can be understood as the result of the formation of charge-transfer complexes. In interpreting the optical absorption data in iodine solutions, Orgel and Mulliken[3] have assumed that iodine would form two classes of complexes with benzene, e.g., the contact and the stable charge-transfer complexes. With

their model, one would expect two peaks in the Raman spectrum of iodine in these solutions. The frequency of the peak corresponding to contact charge-transfer complexes would shift with the benzene concentration more rapidly, and the relative intensity of the two peaks would change. This is contradictory to what we have observed except in mesitylene at low concentrations. However, as Orgel and Mulliken have pointed out,[3] there is a priori no justification for dividing the complexes strictly into two classes. In fact, from the physical point of view, it should be more appropriate to use interaction potentials rather than reaction equilibrium to describe interactions between molecules.

Let $V(\underset{\sim}{r})$ be the change in the potential seen by the iodine molecule at O when an n-hexane molecule at $\underset{\sim}{r}$ is replaced by a benzene molecule. The first- and second-order derivatives of V with respect to the normal coordinate of vibration will then induce a shift $\Delta(V)$ in the vibrational frequency of iodine.[8] with N benzene molecules, the iodine vibration would have in the first order a resonance frequency

$$\omega_o = \omega^o + \sum_{i=1}^{N} \Delta(V(\underset{\sim}{r}_i)). \tag{1}$$

The spectral distribution of the vibration one would observe is then given by

$$S(\omega) = \int g(\omega - \omega_o(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N))\, f(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N)\, d\underset{\sim}{r}_1 \ldots d\underset{\sim}{r}_N \tag{2}$$

where g is the line-shape function and $f(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N)$ is the N-particle distribution function. The interpretation can however be greatly simplified if we consider the mean frequency $\langle\omega_o\rangle$ rather than the spectral distribution of the line. We find

$$\langle\omega_o\rangle = \int_0^\infty S(\omega)\omega\, d\omega$$
$$= \langle\omega^o\rangle + \langle\Delta\rangle \tag{3}$$

where $\langle\omega^o\rangle$, independent of V, is the mean frequency of the line in the absence of benzene, and if $\rho(\underset{\sim}{r})$ is the number of benzene molecules per unit volume at $\underset{\sim}{r}$, the mean frequency shift $\langle\Delta\rangle$ of the line is given by

$$\langle\Delta\rangle = \int \Delta(r)\ \rho(r)\ 4\pi\ r^2\ dr. \tag{4}$$

In the neighborhood of the iodine molecule at 0, the density $\rho(r)$ is different from the average density ρ_o. A benzene molecule at $\underset{\sim}{r}$ sees a potential change of $V_{BI}(\underset{\sim}{r})$due to the presence of the iodine molecule, and of $\int' V_{BB}(\underset{\sim}{r} - \underset{\sim}{r}')\ \rho(\underset{\sim}{r}')d\underset{\sim}{r}'$ due to other benzene molecules substituting the n-hexane molecules, where the integration $\int'$ $d\underset{\sim}{r}'$excludes the space in the repulsive range of the benzene molecule at $\underset{\sim}{r}$, and for $\rho(\underset{\sim}{r}) = \rho_o$, we expect $\int' V_{BB}(\underset{\sim}{r} - \underset{\sim}{r}')\rho_o\ d\underset{\sim}{r}'$ to be independent of $\underset{\sim}{r}$. Here, we have neglected for simplicity the further complication due to relative orientation of molecules. We (can) assume that the benzene-benzene and the benzine-iodine interactions are highly directional along the axis of the benzene ring. We now have

$$\rho(\underset{\sim}{r}) = (\rho_o/Z)\ \exp\ \{(-1/kT)[\int' V_{BB}(\underset{\sim}{r} - \underset{\sim}{r}')\ \rho(\underset{\sim}{r}')d\underset{\sim}{r}' + V_{BI}(\underset{\sim}{r})\ ]\}$$
$$Z = \int_{\text{unit volume}} \exp\ \{(-1/kT)[\int' V_{BB}(\underset{\sim}{r} - \underset{\sim}{r}')\ \rho(\underset{\sim}{r}')d\underset{\sim}{r}' + V_{BI}(\underset{\sim}{r})]\}\ d\underset{\sim}{r}. \tag{5}$$

Using the iteration approximation, and neglecting the difference between $\rho(\underset{\sim}{r})$ and ρ_o in Z, we find, from Eqs. (4) and (5)

$$\langle\Delta\rangle = \int_{r_o}^\infty 4\pi r^2\ \Delta(r)\ (\rho_o/Z_I)\ \exp\ \{(-1/kT)[\rho_o h(r) + V_{BI}(r)]\}\ dr \tag{6}$$

where

$$Z_I = \int_{\text{unit volume}} \exp(-V_{BI}/kT)d\underset{\sim}{r}$$

$$h(r) = \int V_{BB}(\underset{\sim}{r} - \underset{\sim}{r}') \{(1/Z_I) \exp[V_{BI}(\underset{\sim}{r}')/kT] - 1\} d\underset{\sim}{r}' \to 0 \quad \text{as} \quad r \to \infty$$

It is difficult to evaluate h(r) in general. We make the simplification by assuming that $[r^2\Delta(r) \exp(-V_{BI}/kT)/h'(r)]$ varies slowly compared with $\exp[-\rho_o h(r)/kT]$. We would then obtain

$$\langle\Delta\rangle = - C [1 - \exp(-\lambda \rho_o/\rho_m)] \tag{7}$$

where

$$C = \frac{4\pi kT}{Z_I} \langle(\Delta/\frac{dh}{dr}) r^2 e^{-V_{BI}/kT}\rangle$$

$$\lambda = \rho_m h(r)/kT$$

and ρ_m is the average density of pure benzene. The curves of $\langle\Delta\rangle$ versus (ρ_o/ρ_m) given by Eq. (7) are plotted in Fig. 1, in comparison with the experimental data. For each curve, the parameters C and λ were chosen to match the initial slope and the maximum frequency shift. The agreement between experimental results and theoretical curves is excellent.

The vibrational frequency shift of iodine with benzene or methylated benzene concentration can therefore be understood as the result of interaction between iodine and benzene or methylated benzene. At the same concentration, the shift will be larger if the interaction potential is stronger and steeper. Thus, from Fig. 1, we conclude that the interaction between iodine and methylated benzenes increases with the degree of methylation. The methyl groups seem to be responsible for the stronger interaction with iodine.[9] Note that we have not yet specified the

physical mechanism for the interaction. However, we expect that in replacing n-hexane by benzene, the change in electrostatic interaction is small. The iodine frequency shift is mainly due to the formation of charge-transfer complexes between iodine and benzene. If the charge-transfer interaction is sufficiently strong and steep, then the model of Orgel and Mulliken should be a good approximation. Equation (2) would also predict the appearance of two well separated peaks in the spectral distribution, one for iodine complexes and the other for iodine molecules shielded by inert solvent. The relative intensity of the peaks depends on the distribution of the methylated benzene molecules. This is what we observed in the case of mesitylene at low concentrations. The same would be true if, for example, pyridine instead of mesitylene is used.

Since our calculation is a first-order one, we expect that the discrepancy between theory and experiments would be larger for stronger interaction. From Eq. (7) we can also predict that if $V_{BI} > kT$, the frequency shift should decrease with temperature. The theory in this paper can also be used to interpret the optical absorption data in iodine solutions.[1-3] Instead of measuring the extinction coefficient at a particular frequency in the charge-transfer band,[2,3] it would be more appropriate to consider the integrated absorption strength for the whole charge-transfer band. Then Eq. (4) would also describe the variation of the charge-transfer absorption with benzene concentration if now $\Delta(\underset{\sim}{r})$ is the induced charge-transfer oscillator strength of an iodine molecule at 0 due to the presence of a benzene molecule at $\underset{\sim}{r}$. Curves similar to Fig. 1 would be expected.

ACKNOWLEDGMENT

This research was supported by the Lawrence Radiation Laboratory through the United States Atomic Energy Commission.

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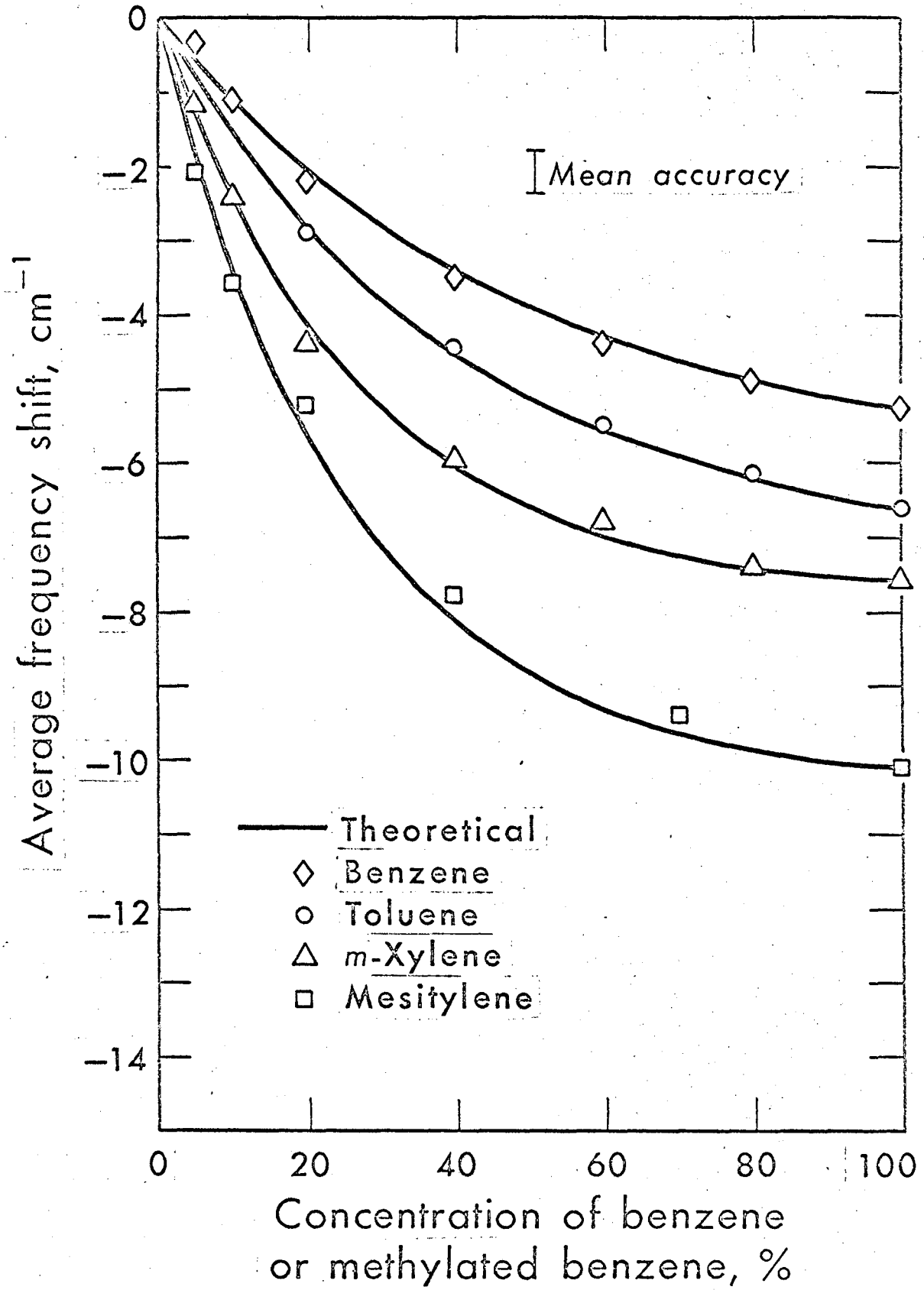

Fig. 1 Average frequency shift of the iodine stretching vibration as a function of the concentration of benzene (or methylated benzene) in the liquid mixture of benzene (or methylated benzene) and n-hexane.

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