

Infrared spectrum of benzene isolated in argon and krypton matrices

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Abstract—The i.r. spectrum of benzene in matrices of Kr and Ar has been determined and shown to be strongly affected by aggregation of the benzene. Sufficient isolation of benzene (Bz) in Ar matrices was not found until the Ar/Bz was 3000 and higher, and isolation in Kr did not occur at the highest dilution possible for us to study (Kr/Bz = 1480). The vibrational frequencies for benzene isolated in the Ar matrix were in good agreement with those measured in the gas phase, but the measured *absolute* intensities disagreed drastically with gas phase measurements (by at least 100%). However, the *relative* intensities for the matrix-isolated benzene sample were in good agreement with gas phase measurements, suggesting that the explanation for the intensity problem lies in the difference in the sticking coefficients for matrix and benzene, so that the concentration of benzene in the sample at the window is unknown. For benzene in Kr matrices accurate absolute intensities were obtained that were in good agreement with gas phase studies when corrected for the effective field factor.

INTRODUCTION

Because molecular vibrational spectra of matrix-isolated systems are characterized by the narrowness of the observed lines, we believe it may be possible to obtain reliable estimates of the absolute intensities of individual bands which overlap badly in the gas phase. These studies could be made fairly readily for the molecule isolated in an Ar matrix, where experimental techniques are well established and when the intensity perturbation by the matrix may be expected to be small [1]. However, the feasibility of this particular application should first be tested on a molecule whose spectra and intensities have been fairly well studied in the various phases. Our study of the absolute intensity of CO in the argon matrix was encouraging [1], but we think further studies should be made of more representative polyatomic molecules in the argon matrix. Benzene is a good candidate for such a trial, since there have been numerous intensity measurements on the gas [2], liquid [3], solid [4], and even glass phases [5], as well as intensity measurements in some systems involving benzene complexed with other molecules [5, 6]. We hoped to determine in this study whether or not the concentration of benzene on the window and the pathlength of the matrix sample could be determined accurately enough so that the i.r. intensities could have some value as an analytical tool.

We are, of course, aware that one of the difficulties in such a study of i.r. intensities of molecules in

matrices is that aggregation of the molecules may occur on condensation, thus changing the spectrum. Furthermore, we must be careful to avoid complexing of the molecule with impurities (such as CO with H₂O [7]) with the resulting change in spectrum. Although there have been numerous studies of stable molecules isolated in matrices (including H₂O in N₂ [8], CO in argon [1], and even benzene [9, 10], together with complexes such as C₆H₆—Br₂ in N₂ [9], CO—H₂O in argon [7], CO—HCl [11], and H₂O—HCl [12]), most of these studies have not attempted to determine whether or not the molecule of interest was indeed fully isolated. In addition the effect of the matrix upon the spectrum of the molecule in question has been largely ignored.

We have therefore undertaken the investigation of the spectrum of benzene isolated in two inert gas matrices: argon and krypton. This particular molecule was selected not only because of the extensive studies already made of its i.r. spectrum [2–6], but also because the recent study of benzene in a nitrogen matrix by FREDIN and NELANDER [9] (in connection with a study of its complexes) and that by SPOLITI, CESARO and GROSSO [10] of benzene presumably isolated in different matrices can be compared with our work.

EXPERIMENTAL

Spectral grade benzene was obtained from Mallinckrodt, and was stored under N₂ in a flask with molecular sieve placed on the bottom to remove H₂O. Benzene (Bz) was then placed in a vial without further purification and the vial attached to a vacuum line. Argon and krypton were

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obtained from Matheson. Each gas had a stated purity of greater than 99% and they were used without further purification. The mixtures were prepared in the gas phase by filling two previously calibrated flasks attached to a vacuum line: one with a known pressure of benzene (measured by a Hg manometer) and the other with a known pressure of argon. The stopcock which separated the flasks was then opened, and the gases allowed to mix over an equilibration period of 24 hr. Mixtures were made at various mol ratios ($\text{Ar/Bz} = 3860, 3000, 722, \text{ and } 470$; $\text{Kr/Bz} = 1480 \text{ and } 722$). The gas mixture from one of the flasks was then deposited on a BaF_2 window kept at a temperature of 25 K by a Spectrim cryocooler (obtained from Cryogenic Technology, Inc.). The temperature of the sample was monitored by a thermocouple attached to the block. The period of time after the block reached temperature and before sample deposition was long enough that the window temperature was believed to be the same as the block. The temperature was carefully monitored during deposition and did not change throughout the entire period of deposition. In addition to the thermocouple a heater was attached to the block so that the temperature of the sample could be varied as the need arose.

In order to determine the thickness of the sample the interference fringes that are observed as the solid film is deposited on the cold window were counted and the path-length was calculated according to the method given by HOLLENBERG and DOWS [4]. The deposition rate was controlled by a micrometer and normally was 50 $\mu\text{m/hr}$ (corresponding approximately to 0.4 mmole/hr). To insure an even deposition of the film the gas mixture passed through a needle opening approx 4 cm in front of the sample window and pointed toward the outer window of the cell. RUDYS [13] has shown that with this configuration the gas diffuses more evenly onto the window so that effects due to uneven film thickness are minimized. In all of the experiments a Perkin-Elmer 621 double beam i.r. spectrometer was employed, using a constant N_2 purge to remove any interference from atmospheric H_2O and CO_2 . The spectral slit width in all cases was about 0.5 cm^{-1} . The spectrometer was calibrated utilizing standard gases and the measured wavenumbers are accurate to $\pm 1 \text{ cm}^{-1}$. The transmittance of the pure argon and krypton films deposited on the BaF_2 window were measured and used to determine T_0 . The transmittance T of the benzene-matrix sample was then measured and the value of $\ln(T/T_0)$ was replotted against the frequency. The areas of these curves were measured using a planimeter to obtain the integrated absorbance.

RESULTS

Argon matrix

Most of the bands that are observed in the i.r. spectrum of pure crystalline benzene are not observed when the molecule is isolated in an inert matrix. The fundamentals that are active for the isolated molecule in the matrix are shown in Fig. 1 and their wavenumbers and intensities are given in Table I. The spectra shown in Fig. 1 are taken from the matrix with the highest Ar:Bz ratio ($\text{Ar:Bz} = 3860$) in order to ensure isolation of the benzene. At such high dilutions, it is difficult to prepare transparent samples that are thick enough to give high optical absorb-

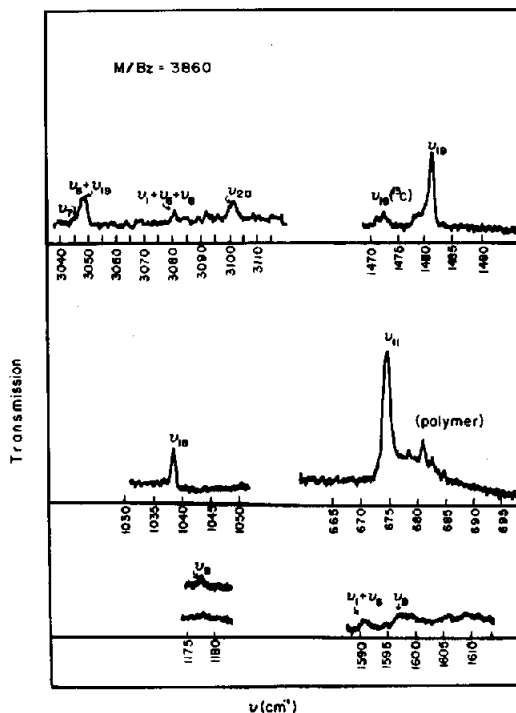


Fig. 1. Benzene fundamentals observed in the i.r. spectrum of benzene in argon matrix at a matrix ratio of $\text{Ar:Bz} = 3860$. (Slit width 0.5 cm^{-1} ; $T = 25 \text{ K} \pm 2 \text{ K}$; $l = 175 \mu\text{m}$.)

ances, so the absorbances shown in Fig. 1 are comparatively low. In addition to the absorption bands shown in Fig. 1, two combination bands at 1807 and 1957 cm^{-1} are also observed to absorb weakly, but no other absorption bands are found for benzene in the argon matrix. As the Ar:Bz ratio is decreased, the spectra remain essentially the same as shown in Fig. 1, except for two features. The first is the e_{1u} mode (ν_{18}) at 1039 cm^{-1} which changes appearance from the singlet shown in Fig. 1 to a doublet at the higher concentrations, as shown in Fig. 2a for $\text{Ar:Bz} = 470$. The second feature is shown in Fig. 2 to involve the a_{2u} out-of-plane CH bending mode, which changes from a sharp single band centred at 676 cm^{-1} in the isolated benzene spectrum (Ar:Bz ratio of 3860) to a broad structureless band centred at 680 cm^{-1} in the concentrated benzene matrix (Ar:Bz ratio of 470). Upon annealing the dilute sample the 674 cm^{-1} band was observed to decrease in intensity with a simultaneous increase in the intensity of the 680 cm^{-1} band, presumably reflecting aggregation of the benzene molecule under the annealing conditions.

In addition to the gas-phase-i.r.-active a_{2u} and e_{1u} modes, modes from one other symmetry species are

Table 1. Observed wavenumbers and apparent intensities (B_i) for benzene (Bz) bands in the gas phase and in Ar and Kr matrices

Band*	Gas phase		Ar matrix		Kr matrix	
	ν^* (cm ⁻¹)	B_i^\dagger (km mol ⁻¹)	ν (cm ⁻¹)	B_i (km mol ⁻¹)	ν (cm ⁻¹)	B_i^\S (km mol ⁻¹)
ν_{20}, e_{1u}	3099	60	3103	—	3096	—
$\nu_1 + \nu_6 + \nu_8, e_{1u}$	3073		3080		3075	
$\nu_8 + \nu_{19}, e_{1u}$	3045		3048		3041	
ν_7, e_{2g}	i	i	3044	—	i	i
$\nu_{17} + \nu_5, e_{1u}$	1964	13	1960	—	—	—
$\nu_{17} + \nu_{10}, e_{1u}$	1807		1808	—	—	—
ν_8, e_{2g}	i	i	1598	—	i	i
$\nu_1 + \nu_6, e_{2g}$	i	i	1592		i	i
ν_{19}, e_{1u}	1485	13	1481	28¶	1479	16¶, ** (12)
ν_9, e_{2g}	i	i	1178	—	i	i
ν_{18}, e_{1u}	1037	8.8	1038	15¶	1036	9¶, ** (7)
ν_{11}, a_{2u}	671	88	674	—	672	—

* From reference [17]; the numbering of fundamentals is taken from MAIR and HORNING, *J. chem. Phys.* 17, 1236 (1949); "i" means inactive. † From [8]. ‡ Apparent integrated intensities from Beer's law plots for matrices at different concentrations. § Values in parentheses corrected for field effect (see [3]). || "—" means "not studied". ¶ Not corrected for field effect. ** From one matrix concentration (Kr:Bz = 1480).

observed to be active in the spectrum of benzene in the argon matrix. These very weak bands occur at 1178, 1592 and 3044 cm⁻¹ (as a shoulder) and are assignable to the e_{2g} fundamental modes. As can be seen in Fig. 1 these bands persist at the lowest benzene concentrations studied. None of the other possible modes of benzene, many of which are observed in the i.r. spectrum of the pure crystal [4], are observed in this experiment.

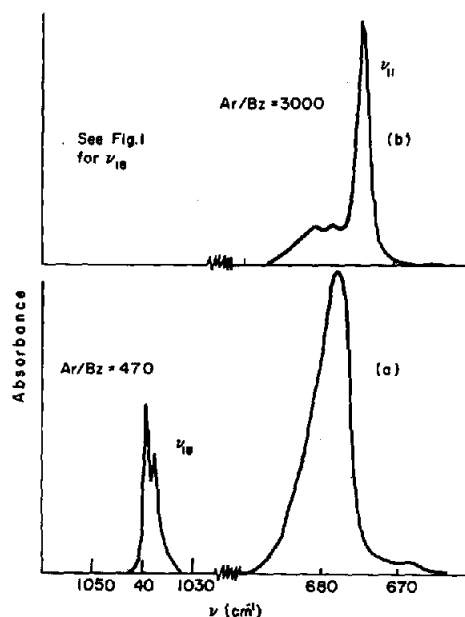


Fig. 2. The e_{1u} ν_{18} mode and the a_{2u} mode (ν_{11}) of benzene in argon (a) at an Ar/Bz ratio of 470, $\ell = 40 \mu\text{m}$; and (b) Ar/Bz = 3000, $\ell = 90 \mu\text{m}$.

The two e_{1u} fundamentals at 1038 and at 1482 cm⁻¹ exhibit little or no change in frequency (except for doubling the 1038 cm⁻¹ band) or in apparent absolute intensity as the concentration is changed. As is shown in Table 2, the ratio of the apparent intensity of the 1482 cm⁻¹ band to that of the 1038 cm⁻¹ band ($B_{19}/B_{18} = 1.98$) is the same as is found in the gas phase (1.89). The intensity of each band is essentially a linear function of concentration in the Beer's law plot, but the resultant apparent absolute intensity (B_i) measured for these two bands is approximately two times that observed for the corresponding bands in the gas phase spectrum (see Table 1). The ratio of the intensity of the a_{2u} fundamental at 680 cm⁻¹ to that of the 1036 cm⁻¹ band for benzene in the Ar matrix ($B_{11}/B_{18} = 8.10$) is also found to be the same as the gas phase value (9.97), within experimental error.

The apparent measured absolute integrated absorption intensity in the C—H stretching region (from 3040 to 3110 cm⁻¹) is also found to be much greater for benzene in the Ar matrix than for benzene in the gas phase. However, as can be seen in Table 2, the ratio of the sum of the intensities of the three observed bands with respect to the intensity of the 1038 band ($B_{CH}/B_{18} = 4.45$) is less than that in the gas phase (8.10) but greater than measured in either liquid (1.63) or solid (1.36) phases.

Krypton matrices

The spectra for benzene in Kr matrices were found to be much broader than for benzene in Ar matrices, but were otherwise similar to those shown in Fig. 1. There were two important differences: only the gas-

Table 2. Relative i.r. intensities (B_i/B_{18}) for the benzene fundamental vibrations for benzene in different environments

Mode	$\nu^*(\text{cm}^{-1})$	B_i/B_{18} values for benzene in							
		gas†	liquid‡	solid§	Ar matrix	Kr matrix	HCl "matrix"¶	Br ₂ "matrix"¶	SO ₂ "matrix"¶
$\nu_{20}, (\nu_{19} + \nu_{18}) \}$ **	3072	8.1	1.6	1.4	4.4	-††	1.1	1.1	2.1
$(\nu_1 + \nu_6 + \nu_8) \}$	1485	1.9	1.7	1.9	2.0	1.7	4.2	1.7	3.2
ν_{19}, e_{1u}	1037	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
ν_{18}, e_{1u}	671	10.0	11.2	5.3	8.1	-††	12	6.9	17
ν_{11}, a_{2u}									

* Gas-phase wavenumbers from Table 1. † Intensity ratio calculated from Table 1; data from SPEDDING and WHIFFEN [2]. ‡ Intensity ratio calculated using data from reference [3]. § Ratio calculated using data from [4, 5]. || This work; ratio calculated using data measured from an Ar/Bz ratio of 3000 and from a Kr:Bz ratio of 722, at 25 K. ¶ Calculated using data summarized in Table 2 of [5a]. ** Fermi resonance triad; average wavenumbers listed. †† Not measured.

Table 3. Wavenumber shifts from gas phase values*: $\Delta\nu_p = \nu_{\text{gas}} - \nu_p$ (p indicates phase or solvent) arranged approximately in order of increasing shifts

Mode	$\nu(\text{gas})^*$ cm^{-1}	Ar matrix†	$\Delta\nu_p$ N ₂ matrix‡	Kr matrix†	Pure solid	Glassy benzene	in HCl	in Br ₂ §
ν_{20}	3099	-4	-1	3	9	13	13	19
$\nu_1 + \nu_8 + \nu_6$	3073	-7	-4	-2	6	11	11	13
$\nu_{19} + \nu_8$	3045	-3	1	4	12	15	14	16
ν_{19}	1485	4	2	6.5	9	10	10	12
ν_{18}	1037	-1.5	$\begin{Bmatrix} -1.1 \\ -2.8 \end{Bmatrix}$	1	1	4	4	5
ν_{11}	671	-3	-7.6	-1	-9	-4	-33	-11
$\nu_{17} + \nu_5$	1964	+9	4	-¶	-13	-1	-17	-8
$\nu_{17} + \nu_{10}$	1807	-1.5	-8	-¶	-25	-13	-37	-22

* [2]. † This work. ‡ [9]. § [6]. || [5a]. ¶ Not observed.

phase-i.r.-active e_{1u} and a_{2u} fundamentals were found in the spectrum of either the dilute or the concentrated benzene-Kr matrix, and no evidence was found for an e_{1g} shoulder in the C—H stretching region for benzene in the Kr matrix.

The apparent absolute integrated molar absorption coefficients, B_i for the bands at 1482 and 1038 cm^{-1} were measured for benzene in the most dilute sample in the Kr matrix (Kr:Bz = 1480) and found to be 15.6 km/mol for the 1482 and 9.1 km/mol for the 1038 cm^{-1} band. These values agree, within experimental error, with the gas phase values of 13.0 km/mol for the former and 8.80 km/mol for the latter band, especially when we estimate some correction for the "field effect" in the matrix (see Table 1). The intensity ratios shown in Table 2 for these fundamentals of benzene in the gas-phase (1.89) and in the Kr matrix (1.7) agree within the experimental error.

DISCUSSION

Although we did not expect to observe any effects due to aggregation at matrix/benzene ratios greater than 500, we believe the spectra in Figs. 1 and 2, especially in the 680 cm^{-1} region, provide evidence

for such effects. From both the concentration studies in Ar and in Kr and the annealing studies in Ar we can reasonably assign the higher frequency portion of the a_{2u} system to absorption by some type of polymeric benzene, while the sharp band at 674 cm^{-1} in Ar is most certainly due to isolated monomeric benzene. Indeed, we believe there is evidence for absorption in this region by polymeric benzene even in the lowest-concentration matrices (Ar:Bz = 3000 and 3600). We believe some aggregation of the benzene even in the most dilute Kr matrix (Kr:Bz = 1480) may account partially for the extraordinary breadth of the spectral bands observed in that system.

Since it seems quite unlikely on a statistical basis that dimer formation would occur at a matrix dilution of 1000, we considered possible explanations, especially since benzene is non-polar with weak attractive forces, compared to water dimers, for example. We do not believe aggregation occurs during annealing after the deposit forms on the cold window, since no further changes are observed over periods as long as 8 hr. We thought it might be possible that the actual concentration of benzene in the matrix was much higher than the measured concentration in the

gaseous mixture, due to the difference in sticking coefficients discussed below in connection with the measurement of absolute intensities. We think it is possible that the true matrix ratio might be 500 instead of 1000, but the observed extent of aggregation seems to be greater than this effect can explain. Another possibility is that aggregation may occur by diffusion occurring at the time of deposition as the molecules freeze into position. Since our deposition temperatures are relatively high (25 K instead of 10 K normally used), it seems possible that diffusion during deposition may occur, although we did try to keep deposition rates slow enough to avoid this process.

In spite of the difficulty with aggregation, we believe we have almost achieved isolation of the benzene molecule in the most dilute matrices (matrix ratio > 3000). At these extreme dilutions the intensity ratios (shown in Table 2 using the 1038 band as a standard) were found to approach those in the gas phase except in the CH stretching region (ν_{20}) where the relative intensity is still only half as large as that in the gas phase, and more than twice as large as found in the pure solid phase. The frequencies of the various bands of benzene isolated in the Ar matrix are in extremely good agreement with those observed in gas phase. The frequency shifts from gas phase for benzene in various environments are summarized in Table 3; the magnitudes support the interpretation that complete isolation of benzene molecules had been achieved in the case of the Ar matrix. The apparent absolute intensities (B_i , Table 1) for benzene in the Ar matrix are about twice as large as the gas-phase values. We believe that the reason for this is that the true benzene concentration in the matrix is about twice that in the gaseous mixture, due to a higher sticking coefficient for benzene than for Ar on the cold window.

The situation for the Kr-Bz system is more confusing. If we correct the measured intensities for the effective field in the lattice (assuming that the index of refraction for solid Kr is 1.40) we calculate apparent absolute intensities in good agreement with the gas-phase values, as shown in Table 1. We believe this agreement suggests that the concentration of the benzene in the Kr matrix on the window is identical with that for the premixed gas mixture in the bulb. If so, we believe the sticking coefficients of benzene and Kr must then be nearly the same. Hence, we expect to be able to achieve a high degree of isolation of benzene in Kr compared to benzene in the Ar matrix. However, the broad bands found in the spectrum of benzene in the Kr matrix, and their positions, suggest that isolation of benzene molecules in the Kr matrix probably was not yet achieved in the most

dilute matrix (Kr:Bz = 1480) we could study. Apparently the Kr matrix is quite porous to benzene, so that a fair amount of diffusion through the matrix occurs while the sample deposits. This seems to be indicated by measurements of the index of refraction of Ar and Kr films as a function of the deposition temperature [14], which suggest that we can expect maximum density for the Ar lattice deposited at the temperature used here, but not for Kr. In view of these difficulties, the good agreement for the intensities of the ν_{18} and ν_{19} bands in the krypton matrix with the corresponding values in the gas phase should probably be taken more as a measure of the insensitivity of these bands to phase changes than as an indication of the degree of isolation of the molecule.

The wavenumbers of the three bands in the C—H stretching region for the matrix-isolated C_6H_6 are quite different from those observed in the solid. (See Table 1, and Table 3). However, the separations between these bands are the same regardless of whether benzene is pure solid or matrix-isolated. Allowing for exciton splitting in the solid, the intensity pattern is also essentially unchanged. Since this system is from a rather complicated Fermi resonance between two combination bands and a fundamental, the implication is that the wavenumber shifts for the combination bands are essentially the same as the shift for the fundamental [15]. If this were not so, we should expect to see a change in the extent of Fermi resonance and an altered intensity pattern.

The appearance of bands that are normally i.r.-inactive gives an indication of the geometry surrounding the site on which the benzene molecule is situated. The bands observed for benzene in the Ar matrix belong to the symmetry representations e_{1u} , a_{2u} , and e_{2g} of the isolated (D_{6h}) molecule. This observed activity corresponds to that expected if the site symmetry of the benzene in the Ar matrix is D_{3h} . The D_{3h} group is a site group of the Ar lattice in its hexagonal-closest-packed (hcp) configuration rather than in the usual face-centered cubic (fcc) form. Impurities such as CO and N_2 have been shown by X-ray diffraction to induce the transition in the Ar crystal from fcc to hcp [16], but those measurements were made at higher concentrations of impurity molecules than for these studies of benzene in the Ar matrix. Nevertheless, we are suggesting here that the very low concentration of benzene has induced this structure change in the Ar lattice. We believe these observations conclusively establish the site symmetry of benzene in the Ar matrix D_{3h} , and that the most likely explanation is that this phase change has indeed occurred.

Finally, we note that the earlier study of benzene in the Ar matrix by SPOLITI, CESARO and GROSSO [10], even though made at a lower temperature (15 K), failed to achieve isolation of the benzene molecules, as judged by the width of the observed bands (broader than found in our work or in [9] in the N₂ matrix) and by the frequencies (which more closely matched those for the aggregated rather than for the isolated benzene species). The most important criterion to ensure maximum isolation would seem to be sufficient dilution during pre-mixing, followed by a careful selection of deposition rate.

CONCLUSIONS

That benzene is a molecule whose vibrational spectrum is sensitive to its environment is perhaps not readily apparent in work on benzene complexes in solution, and has only recently been realized by FREDIN and NELANDER [9] in their work on benzene complexed with halogens studied in the N₂ matrix. In solution the sensitive a_{2u} mode is very broad, and changes that occur as a result of adding a perturbing molecule to the system are difficult to observe, compared to similar studies in a matrix. One must be careful to ensure that the molecule under consideration, in this case benzene, is indeed isolated in analytical matrix studies and that the observed spectrum is really due to the isolated molecule.

We believe that it is sometimes possible to make accurate measurements of absolute intensities for molecules isolated in matrices (for example CO in argon [1]), but this study of benzene in argon and krypton emphasises some of the difficulties that must be anticipated. Nevertheless, we believe some results can be achieved by careful work. Even these scanty results may prove fascinating; compare, for example, the values of the relative intensities and frequencies measured for benzene fundamentals in different matrices summarized in Tables 2 and 3. Even though ideal conditions have not been achieved, and isolation probably did not occur in the studies of benzene in HCl, SO₂ and Br₂ matrices reported [5a] in Tables 2 and 3, we believe the trends shown in those tables are of considerable interest, and we think they sup-

port the concept of the Ar matrix as a weakly interacting host environment for the benzene guest.

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