Estimates of Dielectric Shifts in Infrared Spectra of Pure Liquids for Use in the Theoretical Evaluation of Vapor Pressure Isotope Effects

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

Observed fundamentals in infrared spectra of pure liquids are red-shifted by the so-called "dielectric effect". This dielectric shift is an excited state effect, and the observed fundamentals must be corrected before one deduces the isotope effects on the zero-point vibrational energy which are needed in the theoretical evaluation of vapor pressure isotope effects. A simple formula is applied to calculate the dielectric shift, which requires only the molar concentration and the integrated absorption coefficient for the fundamental.

I. Background on Vapor Pressure Isotope Effects

A cell model of a molecular liquid is often employed in theoretical considerations on vapor pressure isotope effects [1, 2]. In this cell model, the degrees of freedom of the N-atomic molecule consist of $3N$-6 ($3N$-5 for a linear molecule) internal molecular harmonic vibrations and of six additional ones (five for a linear molecule) which are harmonically bound to the cell and which correspond to translational and rotational motion. The contribution to the vapor pressure isotope effect of the $3N$-6 internal vibrational motions can usually be well expressed just in terms of the isotope effect on the zero-point energy difference between these motions in the gas phase and in the liquid phase. Moreover, this quantity is frequently deduced from the observed fundamentals in the liquid phase and in the gas phase. Often the observed fundamentals are converted into appropriate force constants for liquid phase and gas phase molecules, and these force constants are then used to deduce isotope effects on the zero-point energy difference between the $3N$-6 internal vibraional degrees of freedom in gas and in liquid.

In a study of $^{13}C/^{12}C$ vapor pressure isotope effects in carbon disulfide, Jancsó and Van Hook [3] found that, when the usual procedure is followed of deducing the isotope effect on the zero-point energy difference between liquid and gas from observed spectral data, they could not rationalize the observed vapor pressure data. However, they concluded, without giving details, that the comparatively large "dielectric shift" (*vide infra*) which has been associated with the asymmetric stretching fundamental of carbon disulfide should be removed when the liquid phase force field is derived; when they followed this procedure they were able to obtain agreement with the experimental results.

II. Background on Dielectric Shifts

When dealing with a molecule in a condensed phase subjected to an outside electric field $\boldsymbol{E}$, it is usual to take into account the interaction of the molecule with its neighbors by replacing the macroscopic field by the local field $\boldsymbol{E}_{\text{local}}$. A formulation of the local field which is often employed is the Lorentz field [4],

$$\boldsymbol{E}_{\text{local}} = \boldsymbol{E} + \frac{4}{3}\pi \boldsymbol{P}, \quad (1)$$

where $\boldsymbol{P}$ is the polarization of the system. Another formulation of the local field is the Onsager formulation [4], the details of which will not be given here.

A number of workers, when considering infrared absorption in a pure condensed phase, have called attention to the fact that the appropriate electric field which must be used in the theory of absorption of electromagnetic radiation is also the local field. In the work typified by reference [5], either

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the Lorentz formulation or the Onsager formulation of the local field has been employed. In this work, the observed absorption coefficient at each frequency is multiplied by a factor depending on the frequency dependent real and imaginary portions of the refractive index to find the spectrum which would have been obtained in the absence of the local field effect. The difference between the two spectra is often called the dielectric effect because the theoretical model of this effect has been based on an absorbing molecule imbedded in a dielectric. The difference between the maximum of absorption in the observed spectrum ν_{max} and in the spectrum in the absence of the local field effect ν_0 is referred to as the dielectric shift, $\nu_{\text{O}} - \nu_{\text{max}}$. The values of this shift $\Delta\nu_{\text{L}}$ and $\Delta\nu_{0}$, calculated with the use of the Lorentz and Onsager fields respectively, are not quantitatively the same but do show qualitative similarities. Dielectric shifts so obtained are not available for many molecules since the relevant experimental data are not available. It is noted that Δ values are normally found to be positive. It should also be noted that the spectrum in the absence of the local field effect usually is not the same as the dilute gase phase spectrum. Thus, the force constant set deduced for internal vibrations of the condensed phase molecule from the observed fundamentals corrected for the dielectric shift will generally differ from the corresponding force constant set of the gas phase molecule.

The work of Crawford and his coworkers typified by [6] differs somewhat from that discussed above. Again experimental data on the complex refractive index of the condensed phase is employed. The real and imaginary parts of the local susceptibility are evaluated and compared with the Van Vleck-Weisskopf model of band shape. Only the Lorentz formulation of $\boldsymbol{E}_{\text{local}}$ has been used. The dielectric shift is among the parameters obtained.

Warner and Wolfsberg [7] have recently carried out an analysis of the effect of $\boldsymbol{E}_{\text{local}}$. They obtained a new absorption frequency ν_{l} in the condensed phase, called by them the macroscopic frequency. This frequency is red-shifted from ν_0 and is expressed in terms of molecular parameters. They also found that the condensed phase absorption should be asymmetric, with the observed maximum ν_{max} not at ν_{l}, but with $\nu_{\text{l}} < \nu_{\text{max}} < \nu_0$.

One of us [8] has recently set up a model of a condensed phase consisting of isotropic harmonic oscillators interacting through instantaneous (but not permanent) dipole moments. In a first-order perturbation approach, it is found that the first excited state of the gas phase molecule becomes a band of states in the condensed phase and that, moreover, only a transition to one state in the lower portion of the band is permitted. With use of arguments which are similar to those used in the derivation of Eq. (1), it is found that the red shift (in cm^{-1}) of the frequency from that of the isolated oscillator is

$$\Delta\nu = \frac{4\pi N}{9hc} \left|\langle\boldsymbol{\mu}\rangle_{\text{gr, exc}}\right|^2 . \qquad (2)$$

The label $\Delta\nu$ is intentionally attached to this red shift because it will be advocated that this quantity be used as an estimate of the dielectric shift. Here N is the molecule number concentration, c is the velocity of light in vacuum, $\langle\boldsymbol{\mu}\rangle_{\text{gr, exc}}$ is the matrix element of the dipole moment $\boldsymbol{\mu}$ between the ground state and the excited state, and $\left|\langle\boldsymbol{\mu}\rangle_{\text{gr, exc}}\right|^2$ stands for the scalar product and contains the sum of all such scalar products if the excited state is degenerate. An integrated absorption coefficient Γ defined [9] by

$$\Gamma = \int a(\nu)\frac{\mathrm{d}\nu}{\nu} \cong \frac{1}{\nu}\int a(\nu)\,\mathrm{d}\nu \qquad (3)$$

is now introduced where $a(\nu)$ is the Beer-Lambert law molar absorption coefficient. For harmonic systems, it can be shown that

$$\Gamma = \frac{8\pi^3 N_0 \left|\langle\boldsymbol{\mu}\rangle_{\text{gr, exc}}\right|^2}{3hc} , \qquad (4)$$

where N_0 is Avogadro's number. Substitution into Eq. (2) gives

$$\Delta\nu = N_{\text{c}}\Gamma/6\pi^2 , \qquad (5)$$

with $\Delta\nu\,(\text{cm}^{-1})$, N_{c} the molar concentration (mol cm^{-3}), and Γ ($\text{cm}^2\,\text{mol}^{-1}$).

Equation (5) is identical to the value obtained for $\nu_0 - \nu_{\text{l}}$ by Warner and Wolfsberg except for an additional multiplicative factor $(n_{\text{b}}^2 + 2)/3$ obtained by the latter. This factor arises from a constant background contribution n_{b} to the refractive index from off-resonance terms; such a term was not considered by Wolfsberg nor did he consider any line-shape arguments which might lead to a difference between ν_{l} and ν_{max}. As already noted in [8], this $\Delta\nu$ expression is quite similar in form to a contribution to the pure condensed phase absorption line width evaluated by Vincent-Geisse [10].

Table I. Comparison of dielectric shifts (cm^{-1}) for various frequencies in a number of pure liquids: $\Delta\nu$ Eq. (5) present calculation, $\Delta\nu_L$ and $\Delta\nu_O$. The identifying frequency value ν (cm^{-1}) is a gas phase value.

Substance	ν	$\Delta\nu$	$\Delta\nu_L$	$\Delta\nu_O$
CS_2	1535	10.3	16^{a}, 14.5^{b}	23^{a}
CCl_4	794	~ 5.7^{k}	8^{c}, 2^{d}, 6^{e}	11^{c}, 6^{d}, 4^{f}
	774	~ 3.0^{k}	6^{c}, 4^{e}	8^{c}
$CHCl_3$	774	6.1	6^{d}, 7^{e}, 12^{a}	9^{d}, 17.5^{a}
	1220	0.7		2^{g}, 0.5^{f}
$CHBr_3$	1149	0.9		1^{f}
CH_3I	533	0.1	−0.4^{h}	
	882	0.3	0.2^{h}	
$SiCl_4$	621	11.3		20^{i}
C_6H_6	673	2.5	4^{e}	5^{i}
	1038	0.2	0^{e}	0^{g,f}
	1486	0.2		0^{f}
C_6F_6	1530	5.2	6.9^{j}	
	1020	~ 3.0^{l}	1.3^{j}	
	1002	~ 3.0^{l}	2.7^{j}	
	315	0.1	0.0^{j}	
$(CH_3)_2CO$	1742	2.0		3^{f}
	1218	1.3		2^{f}

[a] Ref. [14]; [b] Ref. [15]; [c] Ref. [16]; [d] Ref. [17]; [e] Ref. [6]; [f] Ref. [18]; [g] Ref. [19]; [h] Ref. [20]; [i] Ref. [21]; [j] Ref. [22].

[k] Overlapping bands in resonance; integrated intensity divided as in Ref. [6] and [16].

[l] Overlapping bands in resonance; integrated intensity divided equally.

Table II. Calculation for various frequencies[a] ν [cm^{-1}] in a number of pure liquids of dielectric shifts $\Delta\nu$ [cm^{-1}, Eq. (5)]. The integrated intensities[a] Γ [cm^2 mol^{-1}] and molar densities[b] N_c [mol cm^{-3}] needed for Eq. (5) are given as well as n_D the index of refraction[b] corresponding to the sodium D line. The densities correspond to 293 K and 1 atmosphere or to the normal boiling point and 1 atmosphere, if the substance is not liquid at 293 K.

Substance	Freq. Desig.	ν	Γ	N_c	$\Delta\nu$	n_D
CO		2143	2700	0.0283	1.29	
HBr		2559	423	0.0342	0.24	1.325
NO		1876	1443	0.0423	1.03	1.330
CO_2	ν_2	667.4	6246	0.025	2.64	
	ν_3	2349	27361	0.025	11.55	
CS_2	ν_2	397	1364	0.0166	0.38	1.6295
	ν_3	1535	36821		10.32	
CSe_2	ν_3	~ 1300	21777	0.0157	5.76	1.845
OCS	ν_2	521	520	0.0206	0.18	
	ν_1	859	2006		0.71	
	ν_3	2062	32234		11.43	
SO_2	ν_2	518	5228	0.0457	4.03	
	ν_1	1151	2060		1.60	
	ν_3	1362	14062		10.92	
C_2H_2	ν_5	730	24583	0.0238	9.90	1.0005
	ν_3	3282	2215		0.90	
H_2CO	ν_6	1167	823^{c}			
	ν_5	1264			~ 0.19	
	ν_3	1500	619		0.28	
	ν_2	1746	3341		1.52	
	ν_1	2783	4463^{c}		~ 0.10	
	ν_4	2843			~ 0.10	
CCl_4	ν_4	314	63	0.0103	0.01	1.4601
	ν_3	794	~ 33000^{d}		~ 5.74	
	$\nu_1 + \nu_4$	774	~ 17000^{d}		~ 2.96	
CF_4	ν_4	632	1940	0.0223	0.73	
	ν_3	1283	80053		29.73	
CH_4	ν_4	1306	2695	0.0291	1.32	
	ν_3	3019	2308		1.17	
$CHBr_3$	ν_5	669	20454	0.0114	3.95	1.5976
	ν_4	1149	4456		0.86	
	ν_1	3042	97		0.02	
$CHCl_3$	ν_6	261	19	0.0124	0.00	1.4459
	ν_3	363	136		0.03	
	ν_2	680	724		0.15	
	ν_5	774	29038		6.08	
	ν_4	1220	3228		0.68	
	ν_1	3034	24		0.00	
CHF_3	ν_6	507	1020	0.0217	0.38	
	ν_3	700	2135		0.78	
	ν_2	1117	75760^{c}		~ 13.9	
	ν_5	1152			~ 13.9	
	ν_4	1372	7087		2.60	
	ν_1	3036	795		0.29	
CH_2F_2	ν_4	529	930	0.0175	0.27	
	ν_2	1070	6189		1.78	
	ν_8	1090	27011		7.75	
	ν_7	1165	3		0.00	
	ν_9	1430	740		0.21	
	ν_1	2949	801		0.23	
	ν_6	3015	1400		0.40	
CH_3I	ν_3	533	365	0.0161	0.10	1.5380
	ν_6	882	949		0.26	
	ν_2	1252	1770		0.48	
	ν_5	1436	686		0.19	
	ν_1	2970	390		0.11	
	ν_4	3060	68		0.02	
$SiCl_4$	ν_3	621	76507	0.0087	11.28	
SiF_4	ν_4	389	29237	0.0159	7.87	
	ν_3	1032	57728		15.50	
C_6H_6	ν_4	673	13105	0.0112	2.48	1.5011
	ν_{14}	1038	852		0.17	
	ν_{13}	1486	879		0.17	
	ν_{12}	3080	1950		0.37	
C_6F_6	ν_4	215	1211	0.0087	0.18	1.3777
	ν_{14}	215	795		0.12	
	ν_{15}	1002	40509^{c}		~ 2.95	
	comb.	1020			~ 2.95	
	ν_{12}	1530	35692		5.24	
$(CH_3)_2CO$	ν_3	1742	8669	0.0136	1.99	1.3588
	ν_{17}	1218	5608		1.29	

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[a] Gas phase frequencies ν and frequency designations as well as integrated intensities Γ are taken from Ref. [11].

[b] Ref. [23].

[c] Integrated intensities equally divided between overlapping bands.

[d] Integrated intensities of overlapping bands divided as in Ref. [6] and [16].

From the comparison of the works of Warner and Wolfsberg [7] and of Wolfsberg [8], it is reasonable to conclude that the dielectric shift results from the excited state band. Thus, the observed spectroscopic fundamentals ν_{max} should be blue shifted by their respective dielectric shifts $\Delta\nu$ before the fundamentals are used for force constant calculations which in turn are used to calculate isotope effects on zero-point energies in the condensed phase. This is just the procedure proposed by Jancsó and Van Hook [3]. Since dielectric shift values ($\Delta\nu_{\text{L}}$ or $\Delta\nu_{\text{O}}$) are easily available for relatively few infrared absorptions, we now advocate the use of $\Delta\nu$ of (5) for the calculation of the dielectric shift. We are ignoring the $(n_{\text{b}}^2+2)/3$ factor of Warner and Wolfsberg as well as the difference between ν_{l} and ν_{max}; to some degree these omissions probably tend to cancel. We advocate the use of (5) mostly as an indicator of the importance of dielectric shifts. Warner and Wolfsberg found empirically that the refractive index of the material of interest for the sodium D line is a good approximation for n_{b}; this index of refraction n_{D} is listed, where easily available, for purposes of information in Table II.

III. Numerical Evaluation of Dielectric Shifts

In the application of (5) in Tables I and II, Γ values obtained from compilations [11] of gas phase absorption data have been used. However, if the dipole matrix elements $|\langle\boldsymbol{\mu}\rangle_{\text{gr,exc}}|^2$ were much different in the condensed phase, the use of condensed phase absorption coefficient values might be considered preferable. Table I lists gas phase frequencies ν, $\Delta\nu$ calculated from (5), and dielectric shift values obtained by various workers from dielectric effect considerations as discussed above either with use of the Lorentz local field, $\Delta\nu_{\text{L}}$, or with the use of the Onsager local field, $\Delta\nu_0$. Since arguments of the type used in the derivation of (1) were used to derive (5), strictly speaking $\Delta\nu$ should be compared only with $\Delta\nu_{\text{L}}$. All the frequencies in both Tables correspond to symmetry allowed fundamentals except for two cases noted in the Tables where there is a resonance between a fundamental and a combination frequency. We note that dipole "forbidden" fundamentals have no dielectric shifts. Table I includes most of the cases for which $\Delta\nu_{\text{L}}$ and $\Delta\nu_{\text{O}}$ values are readily available. In Table II, $\Delta\nu$ values are listed for many frequencies for which dielectric shifts have not previously been calculated or estimated.

Table I indicates qualitative, if not quantitative, agreement between $\Delta\nu$ and $\Delta\nu_{\text{L}}$ and $\Delta\nu_{\text{O}}$. We conclude from Table I that $\Delta\nu$ reasonably estimates dielectric shifts.

The largest shifts calculated in Table I are those for the ν_3 asymmetric stretching frequency in carbon disulfide and for the ν_3 asymmetric stretching frequency in $SiCl_4$. Table II indicates a number of other frequencies where there are shifts which are equally as large. Fluorine containing compounds appear to have large shifts especially for stretching modes involving F. It is to be noticed that frequencies which can be described as carbon-hydrogen stretching frequencies tend to have very small $\Delta\nu$ values. Thus, the suggestion of Jancsó and Van Hook [12], in their study of vapor pressure isotope effects of benzene, that all the dielectric effects be arbitrarily placed into a carbon-hydrogen stretching fundamentals may be questioned. In their recent study of vapor pressure isotope effects on fluoroform, Ishida and his coworkers [13] stated that no information on dielectric shifts was available; such data are now available in Table II. One can now re-evaluate appropriate vapor pressure isotope effect data on the basis of Table II. We emphasize that it may be possible to obtain "better" $\Delta\nu$ values within the framework of (5) by more critical evaluation of experimental data [11]. It would also be easy to extend Table II with the use of presently available experimental intensity data.

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