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Isotope Effects on Intermolecular Interactions and
Isotopic Vapor Pressure Differences*

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Max Wolfsberg

Chemistry Department, Brookhaven National Laboratory,
 Upton, L. I., New York, U.S.A.

For the present purposes, the condensed phase will be taken to be crystal-like while the corresponding gas phase in the equilibrium will be taken to be a perfect gas. The calculation of an isotope effect on vapor pressure will then involve a knowledge of the internal (or intramolecular) gas phase vibrational frequencies (assumed to be known) of the isotopic molecules and a like knowledge of the corresponding frequencies in the condensed phase, where they may be shifted from their gas phase values, plus a knowledge of the lattice frequencies. This communication deals with some problems in the calculation of isotope effects on the vibrational frequencies of the condensed phase. Whenever possible numerical analysis will be carried through.

The isotope effect on intramolecular frequencies due to dispersion or van der Waals forces between symmetric non-polar molecules will be considered first. This problem has previously been considered by Baertschi and Kuhn on the basis of a Drude model. The present discussion which is based on a second order perturbation treatment clarifies certain points in the problem. The van der Waals interaction is an induced dipole-induced dipole interaction between a pair of molecules which arises in second order perturbation theory. Take a non-vibrating molecule. If a coordinate Q_1 in one of the

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molecules is stretched by an amount ΔQ_1 from its equilibrium value, one obtains a molecule with a dipole moment $(\partial \vec{\mu} / \partial Q_1) \Delta Q_1$. The perturbation operator of the van der Waals interaction now gives in second order perturbation theory a new dipole-induced dipole interaction term which decreases the energy and which is proportional to $|(\partial \vec{\mu} / \partial Q_1)|^2 (\Delta Q_1)^2$. The sum of the coefficients of the terms in the energy expression proportional to $(\Delta Q_1)^2$ are identifiable as the force constant of the motion corresponding to ΔQ_1 . The diagonal force constant F_{ii} of Q_1 is thus lowered by a factor proportional to $|(\partial \vec{\mu} / \partial Q_1)|^2$. These shifts in the diagonal force constants will then lead to isotope dependent shifts in the frequencies. The zero-point energy shift calculated in this manner is the same as that obtained by a more conventional second order perturbation treatment dealing with vibrating molecules and permitting excitation of vibrational states. An isotope effect on the vapor pressure will result. However, since only an isotope independent shift in the harmonic force constants of the intramolecular motion is involved, this effect cannot result in different intermolecular distances for different isotopic species.

To avoid the laborious and complicated procedure of solving secular equations, it becomes worthwhile to evaluate the thermodynamic isotope effect due to these shifts in force constants as a first order quantum correction. With some manipulation, one finds that the contribution of the frequency shifts to the vapor pressure ratio is given by $\ln p_1/p_2 = 1 - (K) \left[\frac{1}{m_{a1}} - \frac{1}{m_{a2}} \right]$ where m_a is the atomic mass of the isotopically substituted atom and K is a positive constant involving the polarizability, the intermolecular separation,

the temperature and isotope independent Cartesian coordinate dipole moment derivatives about which information may be gained from infrared intensities. It is seen that the effect leads to a lower vapor pressure for the lighter species. It is fairly straightforward to apply the above equation to specific cases and one finds that in XY_4 a much larger effect is obtained for X substitution than for Y substitution.

The above isotope effect arises from a Taylor expansion of the dipole moment of the molecule in terms of the vibrational coordinates. The electronic polarizability of a molecule which was assumed to be independent of isotopic substitution above may likewise be expanded in the form $\alpha_0 + \alpha' \Delta Q + \frac{\alpha''(\Delta Q)^2}{2} + \dots$. Only one degree of freedom is assumed here. In first order vibrational perturbation theory, interactions involving α , such as the van der Waals interaction, will then contain terms proportional to $\alpha' \overline{\Delta Q} + \frac{\alpha''}{2} \overline{\Delta Q^2}$ where the bar denotes an average over the vibrations of the molecule. These energies contribute to the zero-point energy of the system. The isotope effect on the vibrational energy change will be proportional to $\alpha' (\overline{\Delta Q_1} - \overline{\Delta Q_2}) + \frac{\alpha''}{2} (\overline{\Delta Q_1^2} - \overline{\Delta Q_2^2})$. The first term will depend on anharmonicity of the vibration for otherwise $\overline{\Delta Q} = 0$. Some knowledge of α' may be obtained from Raman intensities. In molecules possessing permanent dipoles, the Taylor expansion of the dipole moment which has already been employed above will lead in first order perturbation theory to isotope dependent zero-point energy shifts due to the dipole-dipole interaction. Similar considerations apply to quadrupole interactions.

Lastly, the problem of isotope effects on the vibrational frequencies in the condensed phase is considered from a somewhat different view. One can learn about the intramolecular frequencies and the lattice frequencies in the condensed phase from a consideration of the frequencies of molecular models with given force constants. Types of models considered for the condensed phase of XY include XYZ molecules (with the mass of Z infinite) and $(XY)_2$ dimers. Consider for instance the stretching modes of the ^{linear} dimer XYYX with a very small stretching force constant between the two Y atoms and a large XY stretching force constant. One frequency is the same as that of the isolated XY molecule. The other intramolecular frequency is increased such that it is increased more for HHHH than for DDDD and more for DHHD than for HDDH. This is the effect one expects on the basis of comparison of the motion of the light atom with that of the heavier atom. R. P. Bell showed that at equal separation between the centers-of-mass of two vibrating hydrogen molecules the Coulomb repulsion between two H_2 molecules is significantly larger than the Coulomb repulsion between two D_2 molecules. This effect is of the same nature as that found here for the second intramolecular frequency. The third stretching frequency of the model must be associated with a lattice vibration. Investigation of other isotope effects in the models also proves instructive.

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