$$3J = \frac{|A_{zz}^E|^2}{36[(\nu_1 - \nu_3) - (\nu_{ni} - \nu_{nk})]} \quad . \tag{4}$$

The average value of $(\nu_1 - \nu_3)$ for three orientations at 10 K equaled 1.494 ± 0.01 MHz. Assuming $|A_{zz}^E| = 189$ MHz, $3J = 835.5 \pm 0.17$ MHz. For the protonated system over similar orientations, $3J = 902$ MHz, where $\nu_1 - \nu_3 = 1.39$ MHZ. A value of 830 MHz given in Ref. 1 is based on some incorrect ENDOR data. The barrier to rotation for a hindered rotor with a three-fold barrier can be deduced by solving the Mathieu equation.[8] For a tunneling frequency of 835.5 MHz, the barrier equals 0.906 kcal mol^{-1}.

It is interesting to compare the tunneling frequency of radical (II) with that of the undeuterated one. Deuteration slightly decreases the tunneling frequency from 902 to 835 MHz, equivalent to an increase in the height of the barrier from 0.889 to 0.906 kcal mol^{-1}. Our result is in agreement with the general trend observed by Clough and his co-workers. Deuteration of MDBP where all the protons other than those in the 4-methyl group results in a decrease of the tunneling frequency from 4.13 GHz to less than 2 GHz[2] and the corresponding increase in the height of the barrier from 450 to 470 cal mol^{-1}. The replacement of the OH hydrogen atom by a deuterium atom in γ-irradiated crystals of MDBP also reduces the 4-methyl group tunneling frequency however by a much smaller amount, from 4.13 to 4.06 GHz at 4.2 K.[3] The similarity of the decrease in tunneling frequency for II and MDBP with only the OH group substituted by OD suggests that substitution of protons with deuterons distant from the carbon containing the unpaired electron decreases $3J$ by only 2 to 10%. However it appears that substitution of protons with deuterons *ortho* to the radical center on an aromatic ring appear to result in a large decrease (>50%) in the tunneling frequency.

The reason for this effect is not completely understood. Presumably a change in the average vibrational amplitude of the C–D bond (shorter) relative to the C–H bond causes a small change in the intermolecular contribution to the tunneling rotation barrier height, a suggestion given previously.[3] Arguments based on a steric factor being dominant[9] due to a small shortening of the C–D bond do not seem applicable as a reduction[10] rather than an increase in the barrier height should have been observed for radical III.

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Thermodynamic partial derivatives

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Thermodynamic partial derivatives, such as $(\partial S / \partial T)_P$, describe the change in a dependent thermodynamic variable (e.g., S) produced by a change in an independent thermodynamic variable (e.g., T) when the remaining independent variables (e.g., P) are held constant.

These changes are carried out quasistatically under conditions of thermodynamic equilibrium. If the collection of thermodynamic partial derivatives is written in a matrix array, the resulting matrix may be considered as a linear susceptibility tensor. For example, for a

simple single component fluid we may write

$$\begin{pmatrix} \delta S \\ \delta V \end{pmatrix} = \begin{bmatrix} \left(\dfrac{\partial S}{\partial T}\right)_P & -\left(\dfrac{\partial S}{\partial P}\right)_T \\ \left(\dfrac{\partial V}{\partial T}\right)_P & -\left(\dfrac{\partial V}{\partial P}\right)_T \end{bmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix} \tag{1}$$

$$= \begin{bmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \end{bmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix}, \tag{2}$$

where

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P,$$

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

and $-(\partial S/\partial P)_T = (\partial V/\partial T)_P$ by the equality of the mixed second partial derivatives of the Gibbs' free energy $G(T,P)$.[1]

It is sometimes necessary to compute linear response functions with respect to a new set of independent thermodynamic variables. This can be carried out in a simple systematic way by exploiting the interpretation of the thermodynamic partial derivatives as matrix elements of a linear susceptibility tensor. For example, to compute $(\partial V/\partial T)_S$, which can be simply derived by conventional procedures, we proceed according to the following algorithm. More complicated examples will be discussed in the remarks following this example.

(1) Rewrite the susceptibility tensor (2) in matrix form as follows:

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{pmatrix} \delta S \\ \delta V \end{pmatrix} = \begin{bmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \end{bmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix}. \tag{3i}$$

(2) Bring all desired independent thermodynamic displacements to one side of the equation, and all remaining displacements to the other side. This is easily done by exchanging the appropriate matrix columns as follows

$$\begin{bmatrix} -V\alpha_P & 0 \\ -V\beta_T & 1 \end{bmatrix} \begin{pmatrix} -\delta P \\ \delta V \end{pmatrix} = \begin{bmatrix} C_P/T & -1 \\ V\alpha_P & 0 \end{bmatrix} \begin{pmatrix} \delta T \\ \delta S \end{pmatrix}. \tag{3ii}$$

(3) Solve for the dependent displacements by multiplying by the appropriate matrix inverse

$$\begin{pmatrix} -\delta P \\ \delta V \end{pmatrix} = \begin{bmatrix} -V\alpha_P & 0 \\ -V\beta_T & 1 \end{bmatrix}^{-1} \begin{bmatrix} C_P/T & -1 \\ V\alpha_P & 0 \end{bmatrix} \begin{pmatrix} \delta T \\ \delta S \end{pmatrix}$$

$$= \begin{bmatrix} -\dfrac{C_P}{TV\alpha_P} & \dfrac{1}{V\alpha_P} \\ V\alpha_P - \dfrac{C_P}{T}\dfrac{\beta_T}{\alpha_P} & \dfrac{\beta_T}{\alpha_P} \end{bmatrix} \begin{pmatrix} \delta T \\ \delta S \end{pmatrix}. \tag{3iii}$$

(4) Write down the desired susceptibility tensor

$$\begin{pmatrix} -\delta P \\ \delta V \end{pmatrix} = \begin{bmatrix} -\left(\dfrac{\partial P}{\partial T}\right)_S & -\left(\dfrac{\partial P}{\partial S}\right)_T \\ \left(\dfrac{\partial V}{\partial T}\right)_S & \left(\dfrac{\partial V}{\partial S}\right)_T \end{bmatrix} \begin{pmatrix} \delta T \\ \delta S \end{pmatrix}. \tag{3iv}$$

Comparison of the individual matrix elements of Eq. (3iii) with the corresponding thermodynamic partial derivatives of Eq. (3iv) leads immediately to $(\partial V/\partial T)_S = V\alpha_P - (C_P/T)(\beta_T/\alpha_P)$.

The following remarks are useful:

(1) This algorithm is applicable to systems described by any number of independent thermodynamic variables.

(2) This algorithm can be used to evaluate partial derivatives that cannot be obtained from ordinary Maxwell relations, as when the independent variables contain a conjugate pair.

(3) This algorithm yields all matrix elements of the susceptibility tensor simultaneously, rather than requiring a new calculation for each thermodynamic partial derivative.

(4) The susceptibility tensor is a symmetric matrix only when the independent thermodynamic variables are either all intensive or all extensive, and the dependent variables are their conjugates.

(5) For a system described by n independent thermodynamic variables, $(2n)!/(n-1)!(n-1)!$ thermodynamic partial derivatives of the form described above may be computed, but only $n(n+1)/2$ of these are functionally independent. For the simple single component fluid, $n=2$ and all 24 thermodynamic partial derivatives may be expressed as functions of any three independent partial derivatives, such as C_P/T, $V\alpha_P$, and $V\beta_T$.

(6) The functional relationships among thermodynamic partial derivatives provided by this algorithm include, as particular cases, many of the thermodynamic relations derivable from the geometric formulation of thermodynamics and the application of the Schwartz inequality and equality.[2]

(7) Linear combinations of thermodynamic variables (e.g., $d\sigma = -dP + mdT$) can be chosen as independent displacements simply by performing a change of basis transformation.[2]

(8) Partial derivatives involving one or more of the thermodynamic potentials among the independent variables may be computed using this algorithm. Such calculations can be carried out in two ways, illustrated by examples.

(a) *Method of augmentation.* The equation relating the change in the potential to the change in its natural variables (e.g., $dH = TdS + VdP$) is included among the set of equations of the form (2). The augmented set of equations is written in matrix form

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -T & 0 & 1 \end{bmatrix} \begin{pmatrix} \delta S \\ \delta V \\ \delta H \end{pmatrix} = \begin{bmatrix} C_P/T & V\alpha_P \\ V\alpha_P & V\beta_T \\ 0 & -V \end{bmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix}. \tag{4a}$$

The algorithm is then applied.

(b) *Method of replacement.* To compute $(\partial G/\partial T)_U$, the changes dG and dU are written in terms of a common set of displacements (including δT). Using Eq. (2) we find easily

$$\begin{pmatrix} \delta U \\ \delta G \end{pmatrix} = \begin{bmatrix} C_P - PV\alpha_P & VT\alpha_P - PV\beta_T \\ -S & -V \end{bmatrix} \begin{pmatrix} \delta T \\ -\delta P \end{pmatrix} . \quad (4b)$$

Application of the algorithm then leads immediately to the result $(\partial G/\partial T)_U = -S - (C_P - PV\alpha_P)/(P\beta_T - T\alpha_P)$.

(9) An extension of this algorithm can be used to relate higher order partial derivatives under a change of independent thermodynamic variables. For example, $(\partial^2 V/\partial S \partial T)$ can be expressed in terms of C_P/T, $V\alpha_P$, and $V\beta_T$ and their first partial derivatives with respect to P and T.

(10) This algorithm (and a similar extension to higher-order derivatives) is applicable also to nonequilibrium steady-state systems. The kinetic coefficients L_{ik} relate changes in the fluxes (δJ_i) and forces (δX_k) by[3]

$$\delta J_i = L_{ik}\,\delta X_k \;. \quad (5)$$

This relation is valid in the nonlinear regime as well as the linear regime, where $J_i = L_{ik}X_k$ and $L_{ik}(H) = L_{ki}(-H)$. The linear response relation (5) is directly analogous to the linear response relation (2). The kinetic coefficients L_{ik} may therefore be considered as matrix elements of a linear susceptibility tensor, and the algorithm applied as described above.

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Laser photodissociation of Na$_2^+$

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In a previous paper from our laboratory[1] the formation of Na$_2^+$ and Na$^+$ in sodium vapor irradiated by laser light tuned to a D-line was reported. The dimer ions were shown to be the products of Na(3p)/Na(3p) associative ionization,[2] but the origin of the atomic ions was uncertain. It was however speculated that the atomic ions were formed by (laser) photodissociation of incipient Na$_2^+$. In addition, unusual behavior of the ion signals in the presence of buffer gases was observed. While the Na$_2^+$ signal decreased with increasing buffer gas pressure, the Na$^+$ signal increased dramatically. It was also found that for the five buffer gases used Ne, N$_2$, Ar, Xe, and N$_2$O, the behavior of the ion signals was independent of the particular gas.

In an effort to better understand the origin of the atomic ions and the effects of buffer gases, we have performed a series of experiments with an Ar$^+$ laser in which Na$_2^+$ ions were formed by sequential photoexcitation and photoionization of dimer molecules[3] present in the sodium vapor. Photodissociation of these ions was then studied as a function of buffer gas pressure. We also performed experiments with a single frequency cw dye laser tuned to the $3s \rightarrow 3p$ atomic transition. The latter experiments, when compared to our earlier results[1] using a multimode cw dye laser, support the hypothesis that the atomic ions result from photodissociation of the dimer ions formed by associative ionization.

The line selected multimode output from a cw Ar$^+$ laser was loosely focused into a collision cell containing sodium vapor at $\sim 10^{14}$ atom/cm^3; the sodium dimer concentration was about 1% of the atom concentration.[4] In the experiments employing a cw dye laser, in which the dimer ions were formed by associative ionization, the atom density was $\sim 10^{13}$ cm^{-3}. Apertures in the ends of the cell provided for entrance and exit of the laser beam; other apertures in the cell were for introduction of vapor, ion extraction, observation of radiation, and introduction and pressure measurement of buffer gases.

The ions formed in the cell were extracted with a weak electric field, mass analyzed with a quadrupole mass filter, and detected with a particle multiplier operated in the counting mode. The dependences of the ion signals on laser power density were determined by attenuating the laser beam with a set of calibrated neutral density filters.

The sequential formation of Na$_2^+$, and subsequent photodissociation, is illustrated on the potential energy curves shown in Fig. 1. Illumination with any of the 514.5, 488.0, 472.7, or 476.5 nm lines of the Ar$^+$ laser with only sodium vapor in the cell produced Na$_2^+$, however Na$^+$ was detected only when a buffer gas was present. Figure 2 shows log–log plots of the ion signals as functions of laser power density using the 488.0 nm line; the buffer gas was helium at 30 μ pressure. The straight lines are least squares fits to the data, and show that Na$_2^+$ and Na$^+$ formation require two and three photons, respectively. Data taken using each of the other three Ar$^+$ lines yielded the same results. The fact that three photons are required for Na$^+$ formation indicates that photodissociation of the Na$_2^+$ is occurring;