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The Dipole Moment and Polarizability in the n-π^* Excited State of Acetone from Spectral Solvent Shifts

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This paper has presented the expression for the frequency shift, including the solvent refractive index and the dielectric constant; the expression has been determined on the basis of a previous paper (This Bulletin, **38**, 1314 (1965)). According to the present theory and E. G. McRae's theory (*J. Phys. Chem.*, **61**, 562 (1957)), the excited state dipole moment of acetone has been estimated to be 0.86 and 1.84 *D* respectively, both being smaller than the ground state value. The results calculated by the present theory show that the excited state polarizability is 163.1×10^{-25} cm^3 and that the solvation energies in the solvents of *n*-heptane, cyclohexane, carbon tetrachloride, ethyl ether, and methyl acetate are less in the ground states than in the excited states.

McMurry1) has identified the 280 mμ band of acetone as a forbidden n-π^* transition involving the excitation of a non-bonding electron of the oxygen atom to an anti-bonding π-orbital between the carbon and oxygen atoms of the carbonyl group. The band shifts to the blue in polar solvents compared with the case in non-polar solvents.2,3) Bayliss and McRae3,4) have stated that the transfer of the electronic charge away from the oxygen will cause the permanent dipole moment to be decreased in the excited state, since the acetone molecule has a dipole with the negative end directed toward the oxygen.

In the present paper, an attempt has been made to estimate the dipole moment and isotropic polarizability in the n-π^* excited state of acetone by the applications of McRae's expression5) and of a new expression, which has derived by the same procedure as in the previous paper,6) to the frequency shifts of the n-π^* transition of acetone.

Theoretical

On the assumption that there are no strong dipole orientation strains among the spherical solute and the spherical solvent molecules, one may obtain the expression for the frequency shift of an absorption spectrum in a very dilute solution by the same procedure as was used in a previous paper6) as follows: Considering an unperturbed solute molecule and the solvent molecules already interacting with one another in the zeroth order approximation, one may write the solvation energy in erg in the ith excited state of the solute as:

$$
\begin{aligned}
E'_i = & -2.378\times 10^{25}\times\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\times\left[\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}\right.\right. \\
& \left.+\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+3\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4} \\
& \left.+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+5\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\right] \\
& \times\left[\frac{2}{3}\cdot\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\cdot(\mu_i^{\mathrm{u}})^2\right. \\
& +1.380\times 10^{-16}(\mathrm{erg}\cdot\mathrm{deg}^{-1})\times T \\
& \times\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\cdot(\alpha_i^{\mathrm{u}}) \\
& +\frac{1}{3}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot(\mu_i^{\mathrm{u}})^2 \\
& \left.+\frac{1}{2}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot\frac{I_i^{\mathrm{u}}\times I_0^{\mathrm{v}}}{I_i^{\mathrm{u}}+I_0^{\mathrm{v}}}\cdot(\alpha_i^{\mathrm{u}})\right] \qquad (1)
\end{aligned}
$$

where M is the molecular weight; d, the liquid density; ε, the dielectric constant; n, the refractive index; I, the ionization potential; T, the absolute temperature; μ, the permanent dipole moment, and α, the isotropic polarizability. Throughout this paper the notations u and v will refer to the solute and the solvent respectively. Here E'_i is taken as negative if the ith excited state energy of the solute is decreased in solution. The solvation energy for the ground state of the solute is obtained by replacing i by 0 in Eq. 1. It is obvious from Fig. 1 that the frequency shift $\Delta\nu_{i0}=\nu_{i0}(\mathrm{soln})-\nu_{i0}^{0}$ (gas) is given by $\Delta\nu_{i0}=E'_i-E'_0$, as is found by Bayliss and McRae.3) The frequency shift in cm^{-1} is given by:

$$
\begin{aligned}
\Delta\nu_{i0} = & -1.198\times 10^{41}(\mathrm{erg}^{-1}\mathrm{cm}^{-1}) \\
& \times\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\times\left[\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\right.
\end{aligned}
$$

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1) H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941).

2) H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **72**, 411 (1951).

3) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

4) N. S. Bayliss and E. G. McRae, ibid., **58**, 1002 (1954).

5) E. G. McRae, ibid., **61**, 562 (1957).

6) T. Abe, This Bulletin, **38**, 1314 (1965).

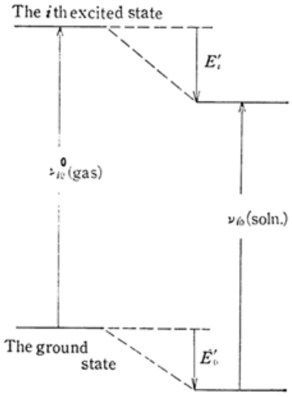

Fig. 1. Formal diagram of the effect of the solvation energies E'_0 and E'_i on the relation between the absorption frequencies in the gas state and in solution.

$$\begin{aligned}
&+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+3\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4} \\
&+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+5\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\Bigg] \\
&\times\left[\frac{2}{3}\cdot\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\cdot\right. \\
&\quad\{(\mu^{\mathrm{u}}_i)^2-(\mu^{\mathrm{u}}_0)^2\}+\boldsymbol{k}T \\
&\times\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\cdot\{(\alpha^{\mathrm{u}}_i)-(\alpha^{\mathrm{u}}_0)\} \\
&+\frac{1}{3}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot\{(\mu^{\mathrm{u}}_i)^2-(\mu^{\mathrm{u}}_0)^2\} \\
&+\frac{1}{2}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot I^{\mathrm{v}}_0\cdot\left\{\frac{I^{\mathrm{u}}_0-\boldsymbol{hc}\nu^0_{i0}}{I^{\mathrm{v}}_0+I^{\mathrm{u}}_0-\boldsymbol{hc}\nu^0_{i0}}\cdot(\alpha^{\mathrm{u}}_i)\right. \\
&\left.\left.-\frac{I^{\mathrm{u}}_0}{I^{\mathrm{v}}_0+I^{\mathrm{u}}_0}\cdot(\alpha^{\mathrm{u}}_0)\right\}\right] \qquad (2)
\end{aligned}$$

where $\boldsymbol{h}$ is the Planck constant; $\boldsymbol{c}$, the velocity of light, and $\boldsymbol{k}$, the Boltzmann constant. For a non-polar solvent the first and second terms in the second square brackets in Eq. 2 are zero. Equation 2 can be further written in the following form:

$$\{(\mu^{\mathrm{u}}_i)^2-(\mu^{\mathrm{u}}_0)^2\}+(\alpha^{\mathrm{u}}_i)\cdot A=B \qquad (3)$$

where

$$\begin{aligned}
A=3\times&\left[\frac{2\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\right. \\
&\left.+\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\right]^{-1} \\
&\times\left[\boldsymbol{k}T\cdot\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\right. \\
&\left.+\frac{1}{2}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot\frac{I^{\mathrm{v}}_0(I^{\mathrm{u}}_0-\boldsymbol{hc}\nu^0_{i0})}{I^{\mathrm{v}}_0+I^{\mathrm{u}}_0-\boldsymbol{hc}\nu^0_{i0}}\right]
\end{aligned}$$

and

$$\begin{aligned}
B=3\times&\left[\frac{2\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\right. \\
&\left.+\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\right]^{-1} \\
&\times\left[\boldsymbol{k}T\cdot\frac{\{\varepsilon^{\mathrm{v}}-(n^{\mathrm{v}})^2\}\{2\varepsilon^{\mathrm{v}}+(n^{\mathrm{v}})^2\}}{\varepsilon^{\mathrm{v}}\{(n^{\mathrm{v}})^2+2\}^2}\right. \\
&\left.+\frac{1}{2}\cdot\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\cdot\frac{I^{\mathrm{v}}_0\times I^{\mathrm{u}}_0}{I^{\mathrm{v}}_0+I^{\mathrm{u}}_0}\right\}\cdot(\alpha^{\mathrm{u}}_0) \\
&-8.351\times10^{-42}(\mathrm{erg\cdot cm.})\times\left(\frac{d^{\mathrm{v}}}{M^{\mathrm{v}}}\right)^{1/3}\times\varDelta\nu_{i0} \\
&\times\left(\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4}\right. \\
&+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+3\left(\frac{M^{\mathrm{v}}}{d^{\mathrm{v}}}\right)^{1/3}\right\}^{-4} \\
&\left.\left.+\left\{\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}+5\left(\frac{M^{\mathrm{u}}}{d^{\mathrm{u}}}\right)^{1/3}\right\}^{-4}\right)^{-1}\right]
\end{aligned}$$

The values of A and B can be calculated from the observed values, so the plot of B against A should be linear; the slope of the straight line will be equal to α^{u}_i, and the intersection of the line at $A=0$ will be equal to $\{(\mu^{\mathrm{u}}_i)^2-(\mu^{\mathrm{u}}_0)^2\}$.

The general expression derived by McRae is written in the approximate form:[5)]

$$\begin{aligned}
\varDelta\nu_{i0}=&(aL_0+b)\cdot\frac{(n^{\mathrm{v}})^2-1}{2(n^{\mathrm{v}})^2+1} \\
&+c\left[\frac{\varepsilon^{\mathrm{v}}-1}{\varepsilon^{\mathrm{v}}+2}-\frac{(n^{\mathrm{v}})^2-1}{(n^{\mathrm{v}})^2+2}\right] \qquad (4)
\end{aligned}$$

where a, b and c are constants characteristic of the solute molecule. Assuming that Onsager's reaction radius is equal to $(3M^{\mathrm{u}}/4\pi\boldsymbol{A}_0d^{\mathrm{u}})^{1/3}$, where $\boldsymbol{A}_0$ is the Avogadro number, one may have:

$$\begin{aligned}
c=&\,2.541\times10^{40}(\mathrm{erg^{-1}cm^{-1}}) \\
&\times(d^{\mathrm{u}}/M^{\mathrm{u}})\cdot\mu^{\mathrm{u}}_0(\mu^{\mathrm{u}}_0-\mu^{\mathrm{u}}_i) \qquad (5)
\end{aligned}$$

Therefore, one can obtain the value of μ^{u}_i from Eq. 5 by the same procedure that Robertson, King and Weigang have used for azulene.[7)] By taking L_0 to be approximately a constant characteristic of the solute molecule, they first found the value of (aL_0+b) from the plot of $\varDelta\mu_{i0}$ against $\{(n^{\mathrm{v}})^2-1\}/\{2(n^{\mathrm{v}})^2+1\}$ in the case of non-polar solvents, because the second term in Eq. 4 is zero in this case. Then, in the case of polar solvents they found the value of c that best reproduced the observed value of $\varDelta\nu_{i0}$.

In Eqs. 2 and 4, the important effect of hydrogen bonding found by Nagakura and Baba[8)] has not been considered.

[7)] W. W. Robertson, A. D. King and O. E. Weigang, Jr., *J. Chem. Phys.*, **35**, 464 (1961).

[8)] S. Nagakura and H. Baba, *J. Am. Chem. Soc.*, **74**, 5693 (1952).

Table I. The n-π^* transition bands of acetone and the data used

No.	Solvent	n^{v}(20°C)	ε^{v}(20C°)	μ_0(D, gas)[9]	I_0, eV.	ν_{i0}, cm^{-1}
	Vapor			2.84	9.92[10]	36200[3]
1	n-Heptane	1.388	1.924	0	10.35[11]	35840[3]
2	Cyclohexane	1.426	2.023	0	9.24[10]	35740[3]
3	Carbon tetrachloride	1.460	2.238	0	11.0[9]	35710[3]
4	Ethyl ether	1.356	4.335	1.18	9.72[10]	36090[13]
5	Methyl acetate	1.362	6.68	1.67	10.51[12]	36290[13]
6	Acetonitrile	1.344	37.5	3.94	12.39[10]	36500[13]

Results and Discussion

The n-π^* transition bands of acetone in several solvents and the other data to be used are listed in Table I. The observed value of α_0^{u} for acetone is 63.3×10^{-25} cm^3.[9]

Assuming that the temperature is 20°C, the author has applied Eq. 3 to acetone. The plot of B against A is shown in Fig. 2. It may be seen in Fig. 2 that all the points except for the point 6 fall close to the straight line. It may be expected that there are strong orientation strains between the acetone and the acetonitrile molecules, because acetonitrile has the large dipole moment of 3.94 D. Equations 1—3 are limited for use in solutions in which no strong dipole orientation strains occur between solutes and solvent molecules. Equation 3, therefore, will not hold sufficiently for the case of acetonitrile. On account of the strain, the point 6 is likely to deviate from the line. From the intersection of the line in Fig. 2 the value of $\{(\mu_i^{\mathrm{u}})^2-(\mu_0^{\mathrm{u}})^2\}$ is estimated to be -7.3267×10^{-36} erg·cm^3. Accordingly, the dipole moment in the excited state due to the n-π^* transition is estimated to be 0.86 D, because the observed value of μ_0^{u} is 2.84 D. From the slope of the line the excited state polarizability is estimated to be 163.1×10^{-25} cm^3.

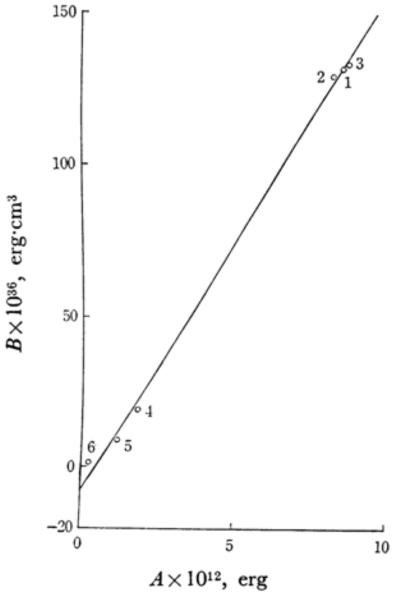

Fig. 2. The plot of B against A.

By applying Eq. 4 in the way mentioned above, the author has obtained the values of -2156 and 983 cm^{-1} for (aL_0+b) and c respectively. From Eq. 5, then, the excited-state dipole moment is obtained as 1.84 D. The frequency shifts calculated are compared with the observed shifts in Fig. 3.

The excited state dipole moment of 0.86 D obtained by Abe's method is considerably smaller than that obtained by McRae's method. This seems to be due to the inclusion of the ground and excited state polarizabilities in the Abe expressions, while the polarizabilities have not been considered explicitly in McRae's expression. The excited state polarizability plays an important role in the frequency shift, because the polarizability is much larger than that for the ground state.

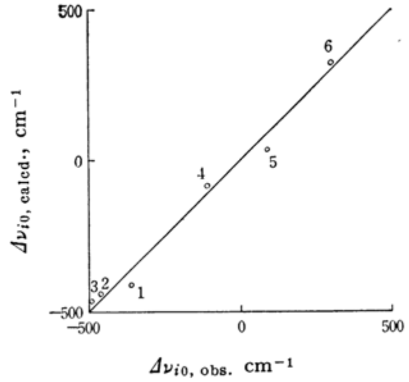

Fig. 3. Calculated vs. observed frequency shifts in n-π^* band of acetone (McRae's method)

According to the above two methods, the n-π^*

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9) Landolt-Börnstein, " Physikalisch-chemische Tabellen." Vol. 1, Part 3, 6th Ed., Springer, Berlin (1951), pp. 386, 395, 509.

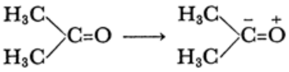
10) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

11) R. E. Honig, ibid., **16**, 105 (1948).

12) K. Higasi, I. Omura and H. Baba, *Nature*, **178**, 652 (1956).

13) M. Ito, K. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.*, **82**, 1317 (1960).

excited-state dipole moment of acetone is considerably smaller than that for the ground state. On the basis of McRae's theory, Ito, Inuzuka and Imanishi[13] have also mentioned that the excited-state dipole moments of ketones are much smaller than their ground-state values. In the ground state of acetone the π electronic charges are distributed more at the oxygen atom than at the carbon in the carboxyl group, because the absolute value of the Coulomb integral for the oxygen atom is larger than that for the carbon atom. The n-π^* transition in acetone transfers a non-bonding electron of the oxygen atom to a π^* orbital distributed over C=O,[3] especially at the carbon atom. The transition is probably represented by:



Consequently, the dipole moment is considerably decreased in the excited state, since the ground-state dipole has the negative end directed toward the oxygen atom.

By putting the above values of $\mu_i^u = 0.86\,D$ and $\alpha_i^u = 163.1 \times 10^{-25}$ cm^3 into Eq. 1, the author has calculated the solvation energies and transition energies of acetone in all the solvents except acetonitrile; they are listed in Table II. The calculated frequency shifts in Table II are in good agreement with the observed shifts in Table I. The differences between the theoretical and the observed values are greater for the polar solvents than for the non-polar solvents. This is probably due to the use of Onsager's approximate expression[14] for the polar-solvent dipole moments. Table II shows that the excited states of acetone are more stabilized than the ground states in the non-polar solvents. These results are contrary to those obtained by Bayliss and McRae's theory.[3,4] According to their theory, the solvation energy in the excited state of acetone is less than the ground-state energy in a non-polar solvent, since the solute dipole moment decreases as a result of the transition. The discrepancy between the present results and Bayliss and McRae's theory seems to be due to the exclusion of the ground- and excited-state polarizabilities in their theory.

TABLE II. THE RESULTS OF CALCULATION OF SOLVATION ENERGIES AND TRANSITION ENERGIES

Solvent	E'_0 cm^{-1}	E'_i cm^{-1}	ν_{i0}, calcd. cm^{-1}
1	− 559	− 921	35840
2	− 695	−1165	35730
3	− 790	−1294	35700
4	− 802	−1007	36000
5	−1118	−1201	36120

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[14] L. Onsager, ibid., **58**, 1486 (1936).