# MANIFESTATION OF DIPOLE-DIPOLE INTERMOLECULAR FORCES IN VIBRATIONAL SPECTRA OF ORGANIC COMPOUNDS

## VI. Brownian Rotational Motion of Molecules in Some Nitriles

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The temperature dependence of line width in the Raman spectra of acetonitrile and benzonitrile in the liquid state was investigated experimentally by photographic and photoelectric methods. By excluding the effect of dipole-dipole broadening from the observed line width, the temperature dependence of the component width due to rotational Brownian motion of the molecules in the liquid was revealed. It was found that the parameters of the rotational Brownian motion undergo sharp changes near the crystallization points of the liquids. To explain this effect it is suggested that molecular association occurs in the liquid at low temperatures under the influence of dipole-dipole forces. By simple calculations, an assignment is made of the frequencies of benzonitrile in the low-frequency region, and the forms of the molecular vibrations are established.

Investigation of the width and form of lines in vibrational spectra as functions of temperature is of great interest from the standpoint of obtaining information on intra- and intermolecular interactions. In [1] it was shown that for polar compounds the width of depolarized lines subject to the highest frequency shift during phase transitions depends on local dipole-dipole intermolecular interaction. The width of such lines in the Raman spectrum can be represented by the following three-term equation:

$$b = b_0 + b_{dip} + b_{br},\qquad(1)$$

where $b_0$ is the residual width—a term which is independent of temperature; $b_{dip}$ is the broadening due to dipole-dipole interaction; $b_{br}$ is the line width due to rotational Brownian motion of the molecules. According to the formula of Sobel'man [2]

$$b_{br} = \frac{1}{\pi c \tau}.\qquad(2)$$

Here $\tau$ is the average time taken for reorientation of the molecules in the liquid. The Frenkel theory [3] gives

$$\tau = \tau_0 e^{\frac{U}{kT}}\qquad(3)$$

where U is the reorientation potential barrier, and $\tau_0$ is the half-period of the rotational oscillations of the molecule. As applied to unsymmetrical deformational vibrations of the molecules, $b_{dip}$ can be defined by the formula proposed in [1]:

$$b_{dip} = \frac{T}{\pi^{3/2}c} \sqrt{\frac{k\,|\varphi'|}{\nu_0 M}\left|\frac{d\nu}{dT}\right|},\qquad(4)$$

where $\varphi'$ is the derivative of the angular coordinate of the molecular dipole moment with respect to the normal coordinate; M is the mass absorption coefficient of the molecule; $d\nu/dT$ is the temperature variation of frequency for the liquid, determined by experiment; k is Boltzmann's constant; $\nu_0$ is the frequency for the gas.

As seen from Eqs. (3) and (4), the last two terms in Eq. (1) depend on temperature. Thus, the value of $b_{br}$, and, consequently, also the values of U and $\tau_0$, can be determined from the temperature dependence of the observed width of the Raman lines and from the value of $b_{dip}$ calculated from experimental data. As known, these values are most important parameters for the motion and interaction of molecules in the liquid phase. Their determination has been the subject of a whole series of spectroscopic investigations. However, the term $b_{dip}$ is not usually taken into account in respect of polar compounds. The present paper is concerned with a spectroscopic investigation into rotational Brownian motion of molecules in strongly polar compounds.

## EXPERIMENTAL

Acetonitrile and benzonitrile were chosen as subjects for the investigation. The investigations were carried out both by a photographic method with the ISP-51 spectrograph and photoelectrically on the DFS-12 spectrometer. The spectral widths of the slits were selected according to the principles described in [4]. For narrow lines, an allowance was made by the Rayleigh method [5] for the distorting effect of the finite width of the slits. It was shown earlier [7] that the greatest temperature-phase shift occurs with the 357 cm$^{-1}$ line of acetonitrile and the 160, 365, and 540 cm$^{-1}$ lines of benzonitrile. (All the Raman line frequencies are related to the gas phase, which we investigated alongside the liquids.) In addition, the 135-cm$^{-1}$ line which we have newly discovered in benzonitrile is also subject to a large shift. This indicates the sensitivity of the above-mentioned lines to intermolecular interaction and determined their selection as subjects for the investigation (see table).

## FREQUENCY ASSIGNMENT

According to [8, 9], the 365-cm$^{-1}$ frequency in the spectrum of acetonitrile corresponds to the deformational vibration of the C≡N group. Various authors [10, 11] have assigned the 160-, 365-, and 540-cm$^{-1}$ frequencies of benzonitrile in different ways. In the transition from gas to liquid the 135-cm$^{-1}$ line is shifted by 27 cm$^{-1}$ toward shorter wavelengths, i.e., it behaves as a deformational frequency of a polar group in monosubstituted benzene [12]. It is natural to assign this frequency to the nonplanar form of the

## Table
## Temperature-Phase Dependence of Line Frequencies and Widths in Raman Spectra of Acetonitrile and Benzonitrile

**Acetonitrile**

| Type of symmetry | Form of vibrations* | Line parameters | Gas 5 atm | Liquid 80° | +50° | +30° | 0° | −20° | −40° | −60° | Crystal −90° | Δν obs. | Δν calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| E | CCN | $\upsilon$, cm⁻¹ | 357 | 375 | 377 | 378 | 380 | 3l2 | 383 | 383 | 387 | 26 | 24 |
|  |  | $b_{obs}$ |  | 17.0 | 14.0 | 11.1 | 9.8 | 8.6 | 7.9 | 7.4 | 3.6 / 2.5 |  |  |
|  |  | $b_{dip}$ |  | 10.9 | 10.2 | 9.3 | 8.4 | 7.6 | 7.0 | 6.4 | 5.3 |  |  |
|  |  | $b_{br}$ |  | 5.1 | 2.8 | 1.8 | 0.6 | 0.2 | 0.1 |  | 0 |  |  |

**Benzonitrile**

| Type of symmetry | Form of vibrations | Line parameters | Gas 7 atm | Liquid 177° | +100° | +50° | +10° | −10° | Crystal −40° | −100° | Δν obs. | Δν calc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $B_2$ | $\nu_{1a}$ | $\upsilon$, cm⁻¹ | 135 | 157 | 160 | 161 | 162 | 162 | 138 | 143 | 27 | 24 |
|  |  | $b_{obs}$ |  |  |  | 8.2 | 7.6 | 7.0 | — | — |  |  |
|  |  | $b_{dip}$ |  | 4.2 | 3.5 | 3.0 | 2.6 | 2.4 | 1,6 | 1,2 |  |  |
| $B_2$ | $\nu_{1b}$ | $\upsilon$, cm⁻¹ | 365 | 378 | 380 | 381 | 383 | 384 | 365 |  | 19 | 15 |
|  |  | $b_{obs}$ |  | 12.0 | 10 2 | 9.3 | 8.6 | 8.0 |  |  |  |  |
|  |  | $b_{dip}$ |  | 4.7 | 3.7 | 3.3 | 2.9 | 2.7 | 1.8 | 1.0 |  |  |
|  |  | $b_{br}$ |  | 4.3 | 3.5 | 3.0 | 2.7 | 2.3 |  |  |  |  |
| $B_1$ | $\nu_{2a}$ | $\upsilon$, cm⁻¹ | 160 | 173 | 175 | 176 | 177 | 178 | 166 / 174 | 164 / 170 | 18 | 26 |
|  |  | $b_{obs}$ |  | 12.5 | 11.2 | 10.4 | 9.3 | 8.5 | 3.3 / 2.2 | 3.2 / 2.2 |  |  |
|  |  | $b_{dip}$ |  | 3.0 | 2.5 | 2.2 | 1.9 | 1.8 | 1.5 | 1.0 |  |  |
|  |  | $b_{br}$ |  | 4.5 | 3.8 | 3.2 | 2.4 | 1.7 |  |  |  |  |
| $B_1$ | $\nu_{2b}$ | $\upsilon$, cm⁻¹ | 540 | 548 | 549 | 550 | 550 | 552 | 543 / 553 | 548 / 557 | 12 | 4 |
|  |  | $b_{obs}$ |  | 3.9 | 3.3 | 2.8 | 2.5 | 2.0 | 0.8 / 1,0 | 0.8 / 1,0 |  |  |
|  |  | $b_{dip}$ |  | 2,0 | 1.7 | 1.5 | 1.3 | 1.2 | 1.0 | 0,8 |  |  |
|  |  | $b_{br}$ |  | 1,9 | 1.6 | 1.3 | 1,0 | 0.8 |  |  |  |  |

*The symbols used for the vibrational forms in benzonitrile are the same as those used in [12] for other monosubstituted benzenes.

C≡N group vibration ($B_2$ symmetry). The 160-, 365-, and 540-cm⁻¹ lines can then be assigned as shown in the table. An important argument in favor of such assignment can be provided by calculations of molecular vibrations, which give both the order of magnitude of the frequency, and the form of the vibration. We will perform the calculation by the simplified method described in [13].

We will represent the acetonitrile molecule in the form of a three-body model with inextensible bonds $l_1$ and $l_2$. We will consider the deformational vibration. We will introduce a vibrational coordinate: $q = \beta_2 - \beta_1$. (The notation for the parameters is clear from Fig. 1.) We define the potential energy as follows:

$$V = \frac{1}{2} K q^2. \tag{5}$$

where $K$ is a dynamic coefficient. The kinetic energy has the following form:

$$T = \frac{1}{2} m_1 \dot{y}_1^2 + \frac{1}{2} m_2 \dot{y}_2^2 + \frac{1}{2} m_3 \dot{y}_3^2 = \frac{1}{2} M \dot{q}^2.$$

From the geometry of the molecular vibrations it follows that

$$\beta_2 = \frac{y_1 - y_2}{l_1}, \quad \beta_1 = \frac{y_2 - y_3}{l_2}.$$

The conservation laws give

$$m_1 \dot{y}_1 + m_2 \dot{y}_2 + m_3 \dot{y}_3 = 0,$$
$$m_1 l_1 y_1 - m_3 l_2 y_3 = 0. \tag{7}$$

Solving these equations with respect to $y_1$, $y_2$, and $y_3$ we find that

$$M = l_1^2 l_2^2 \left( \frac{l_1^2}{m_3} + \frac{l_2^2}{m_1} + \frac{(l_1 + l_2)^2}{m_2} \right)^{-1}.$$

The frequency is clearly determined by the equation

$$\omega^2 = \frac{K}{M}$$

If the value $\omega_j$, taken from experiment, is substituted here, we obtain $K = 0.3 \cdot 10^6$ dyn·cm, which almost coincides with the value of the quasi-elastic coefficient for molecules of the class under consideration [14]. This proves the validity of the assignment. (The assignment of the acetonitrile frequencies is well known from the literature; the calculation given reveals the form of the vibration required for determination of $b_{dip}$.)

We represent the benzonitrile molecule, like other monosubstituted benzenes [13], as a mechanical model with a rigid nondeformable nucleus of mass $m_1$ and moments of inertia $I_y$ and $I_z$ (Fig. 1). We define the potential energy by the expression

$$V = \frac{1}{2} K_1 \alpha_1^2 + \frac{1}{2} K_2 \alpha_2^2. \tag{8}$$

The kinetic energy takes the following form:

$$T = \frac{1}{2} m_0 \dot{z}^2 + \frac{1}{2} I_1 \dot{\beta}_1^2 + \frac{1}{2} I_2 \dot{\beta}_2^2 = B_{11} \dot{\alpha}_1^2 + B_{22} \dot{\alpha}_2^2 + B_{12} \dot{\alpha}_1 \dot{\alpha}_2, \tag{9}$$

where $z = z_2 - z_1$, $m_0 = m_1 m_2/(m_1 + m_2)$, $I_1 = I_z$ or $I_y$ for planar and nonplanar vibrations, respectively, and $I_2 = I_{C\equiv N}$. With the geometrical relationships

$$\begin{cases} \beta_2 = a_1 + a_2 + \beta_1 \\ z = a_1\beta_1 + r(a_1 + \beta_1) + a_2\beta_2 \end{cases} \quad (10)$$

and the conservation law

$$I_1\beta_1 + I_2\beta_3 + m_0 zc = 0 ,$$

$\beta_1$, $\beta_2$, and $z$ can be expressed through $\alpha_1$ and $\alpha_2$. After simple rearrangements, and taking account of Eq. (9), we find that

$$B_{11} = m_0 a_1^2 + I_1 + \frac{(m_0 a_1 c + I_1)^2}{m_0 c^2 + I_1 + I_2} ,$$

$$B_{22} = m_0 a_3^2 + I_2 + \frac{(m_0 a_2 c + I_2)^2}{m_0 c^2 + I_1 + I_2} ,$$

$$B_{12} = -\left[ m_0 a_1 a_2 - \frac{(m_0 a_2 c + I_2)(m_0 a_1 c + I_1)}{m_0 c^2 + I_1 + I_2} \right].$$

By making use of Lagrange equations of the second type the expressions for the kinetic and potential energies lead to a system of two homogeneous linear equations with respect to $\alpha_1$ and $\alpha_2$. Each root of the secular equation corresponds to a normal vibrational frequency $\omega_i$ ($i = 1, 2$) and a vibrational form

$$\left(\frac{\alpha_1}{\alpha_2}\right)_i = -\frac{K_1 - \omega_i^2 B_{11}}{\omega_i^2 B_{22}}. \quad (11)$$

Expressing T in the form of a function of a certain independent coordinate $q_i$

$$T = \sum \frac{1}{2} M_i q_i^2 ,$$

and by taking account of Eq. (11), we obtain all the $M_i$ values. The quasi-elastic coefficients $K_i$ have the same order of magnitude as in other compounds of the $C_6H_5 \cdot CR$ type [13], which confirms the validity of the assignment.

In [15], to check the frequency assignment, use was made of the fact that the frequencies in the liquid for various vibrational forms are variously sensitive to intermolecular interaction. The table gives the observed frequency shifts during the transition from gas to liquid. According to the theory in [17], the frequency shift is determined by the equation

$$\Delta \nu = \frac{|\varphi'|^2}{4\pi^2 c^2 \nu_0 M} |V_0|, \quad (12)$$

where $V_0 = s(\mu^2/R^3)$ is the energy of intermolecular interaction (R is the intermolecular separation, determined for example from the van der Waals corrections), and s is the degree of mutual orientation of the molecules [6]. As seen from the table, calculation by Eq. (12) leads to agreement, with a tolerable degree of error, with experiment. We thereby obtain further conformation for the validity of the interpretation of the spectrum given above.

## ANALYSIS OF LINE WIDTHS

a) Dipole-dipole broadening. The $b_{dip}$ term in Eq. (1) arises from interaction energy fluctuations of the vibrating molecular dipoles [1]. A decisive role is played here by the value of $\varphi'$ [see Eq. (4)]. It is clear that during the molecular vibration the rotation of $\varphi$ of the full dipole moment of the molecule in space depends on the angle of rotation of the bond dipole moments. The dipole moment of acetonitrile can be represented as the sum of the dipole moments of the groups $\mu_{CH_3}$ and $\mu_{C\equiv N}$. Assuming that, as in most
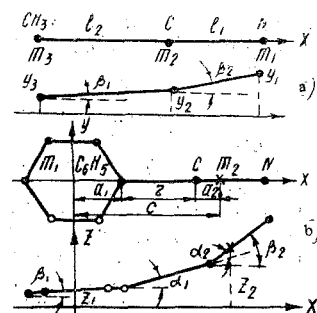


Fig. 1. Models of acetonitrile (a) and benzonitrile (b) molecules; the point indicated by a cross is the center of gravity of the $C\equiv N$ group.

compounds, $\mu_{CH_3} = 0.4$ D and $\mu_{C-C} = 0$, we obtain $\mu_{C\equiv N} = 3.5$ D. In the benzonitrile molecule, the benzene ring is polarized under the influence of the $C\equiv N$ group. Assuming that $\mu_{C\equiv N}$ and $\mu_{C-C}$ are here the same as in acetonitrile, and taking account of the full moment of benzonitrile, $\mu = 4.39$ D, we obtain the dipole moment of the nucleus $-\mu_{C_6H_5} = 0.9$ D. The dipole moments of acetonitrile and benzonitrile thus consist of two principal components:

$$\mu = \mu_1 + \mu_2,$$

where $\mu_1$ is $\mu_{CH_3}$ or $\mu_{C_6H_5}$, respectively; $\mu_2 = \mu_{C\equiv N}$; $\varphi'$ arises from simultaneous rotations of the two components in space. It is clear that the increase in the dipole moment during a small rotation is given by

$$\Delta\mu = \Delta\mu_1 + \Delta\mu_2.$$

For purely deformational vibrations

$$\Delta\mu = \mu \sin\beta \simeq \mu\beta,$$

where $\beta$ is the angle of deviation from the symmetry axis of the molecule. Consequently

$$\varphi' = \frac{\partial\varphi}{\partial q} = \frac{\mu_1}{\mu}\beta_1' + \frac{\mu_2}{\mu}\beta_2'. \quad (6)$$

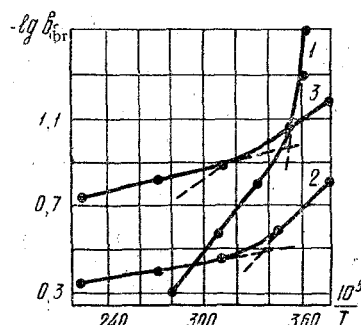The values of $\beta_1$ and $\beta_2$ are readily obtained from Eq.



Fig. 2. Observed temperature dependence of Brownian line broadening: 1) 357 cm$^{-1}$ line for acetonitrile; 2) and 3) 160 and 540 cm$^{-1}$ lines for benzonitrile.

(7) for acetonitrile and from the set of equations (10) for benzonitrile after expressing all the other variables through the corresponding normal coordinate $q_i$. Calculation of $b_{dip}$ by Eq. (4) gives the values presented in the table.

b) **Brownian line widths.** The value of $b_{br}$ can be determined by means of Eq. (1) on the basis of observed values of the width b and the calculated value of $b_{dip}$. The residual width $b_0$ which occurs in Eq. (1) we determine as the difference between the observed line width in the crystal (or liquid at a sufficiently low temperature) and $b_{dip}$ for the given temperature, by taking account of the fact that Brownian rotational motion does not occur in the crystal (or low-temperature liquid) and the temperature dependence of the line width in the crystal (if it occurs) arises from the dipole-dipole interaction. Elimination of $b_{dip}$ gives the $b_{br}$ values shown in the table. The results are presented graphically in Fig. 2.

## DISCUSSION OF RESULTS

It is natural to attempt an explanation of the experimentally observed temperature dependence of the width of depolarized Raman lines in the investigated compounds on the basis of the idea put forward by Frenkel on the rotational Brownian motion of molecules in the liquid phase. Here the theoretical equations (2) and (3) give a linear relationship between $\log b_{br}$ and $1/T$. However, it must be emphasized here that this conclusion is obtained on the assumption that the potential barrier of the reorientations U and the half-period of the rotational oscillations of the molecule $\tau_0$ in the liquid remain unchanged. Most papers contain this assumption; at the same time it can be considered proved only for nonpolar and low-polarity compounds.

Turning to the data obtained in the present work, we see (Fig. 2) that in the case of acetonitrile and benzonitrile, within the limits of experimental error, there is in fact a linear relationship between the above-mentioned quantities, but it is only fulfilled in limited temperature ranges. Thus, for the 357-cm$^{-1}$ line of acetonitrile, the experimental points lie on a straight line in the high-temperature range, but the curve turns sharply upward at about 10–0° C. It then straightens out again in the low-temperature range (approximately from 0° C to the melting point). This creates the impression that there is a break in the curve in a narrow temperature range—near 0° C. According to Eqs. (2) and (3), the slope of the curve determines the value of the potential barrier U, and the intercept made on the ordinate axis by its continuation determines the value of $\tau_0$. The break in the curve leads to the idea of a rapid change in both these values near the above-mentioned temperature; both the reorientation value and the frequency of the rotational oscillations of the molecule increase with decrease in the temperature of the liquid. Determination of U for acetonitrile in the high-temperature range gives a value on the order of 3 kcal/mole and $\tau_0 \simeq 10^{-14}$ sec. The first of these values increases by 2–3 times in the low-temperature region. (Unfortunately, the experimental error does not allow these values at low temperatures to be determined

with sufficient accuracy.) A similar effect can also be seen in the case of benzonitrile (the temperature behavior of the 160-cm$^{-1}$ and 540-cm$^{-1}$ lines in Fig. 2). The bend in the curve is less distinct here, but it is fairly clear and is observed at a temperature of 20–10° C. It is difficult to determine the values of U and $\tau_0$ for benzonitrile with any certainty, since there are no reliable data on the degree of depolarization of these lines.*

It seems to us that the changes observed in the nature of the temperature dependence of the line widths for acetonitrile and benzonitrile indicate that changes occur in the structure and in the nature of the intermolecular interaction and the motion of the molecules in the liquid as it approaches the crystallization point. Such change evidently precedes the freezing of the rotational Brownian motion of the molecules which takes place in the crystalline phase. It can be supposed that in the investigated polar liquids at low temperatures there is dipole-dipole association of the molecules, and that this on the one hand hinders the rotational transitions of the molecules and on the other leads to an increase in the intermolecular quasi-elastic constants for the rotational oscillations (decreased $\tau_0$). The change we found in the properties of polar liquids on approaching the crystallization point correlate well with other well-known anomalies of liquids at low temperatures.

In conclusion we mention that consideration of the effect of dipole-dipole intermolecular forces on the line widths has made it possible to obtain information on the nature of the rotational Brownian motion of molecules in nitriles on cooling.

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*The relationship between $b_{br}$ and $\tau$ in the form represented in Eq. (2) is only valid for completely depolarized lines. Corrections need to be introduced for lines which are partly depolarized [16].

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