[4] W. H. Evans, R. Jackobson, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. Std. **55,** 83 (1955).

[5] Preliminary evidence for these features was first reported by C. B. Ellis, J. H. Simpson, and D. S. Bayley, AD-624481, November 1965 (available from Clearinghouse for Federal Scientific and Technical Information).

[6] G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950), 2nd ed.

[7] F. W. Loomis and S. W. Niles, Phys. Rev. **32,** 873 (1928).

[8] T. Carroll, Phys. Rev. **52,** 822 (1937).

Light Scattering from Chemically Reacting Mixtures

Bruce J. Berne
Department of Chemistry, Columbia University
New York, New York

AND

J. M. Deutch* and James T. Hynes†
Department of Chemistry, Princeton University,
Princeton, New Jersey

AND

H. L. Frisch
Department of Chemistry, The University of the State of New York at Albany, Albany, New York

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In a recent communication it was shown how light scattering can be used as a probe of fast reaction kinetics. Although the major conclusions of that communication are unaltered, an error was made in relating fluctuations in the dielectric constant to composition fluctuations. In this note the error is repaired and the original reasoning is clarified.

We consider the spectral distribution of light scattered from an equilibrium ternary mixture in which two of the components S_1 and S_2, present in small concentrations, are in dynamic equilibrium.

In this analysis only the effect of composition fluctuations is considered. We neglect the effects of density (or pressure) fluctuations. This may be a severe approximation. To our knowledge the combined effects of composition, temperature, and density (or pressure) fluctuations have not yet been taken into account.[1,2]

The intensity of scattered light $i(\mathbf{k}, \omega)$ is proportional to the real part of the space–time Fourier transform of the autocorrelation function of the dielectric constant $i(\mathbf{k}, \omega) \propto \mathrm{Re}\langle\delta\bar{\epsilon}(\mathbf{k}, \omega)\delta\epsilon(-\mathbf{k}, 0)\rangle$. (We use the notation of Ref. 3.)

Composition fluctuations give rise to fluctuations in the dielectric constant

$$\delta\epsilon(\mathbf{r}, t) = (\partial\epsilon/\partial C_1)_0\delta C_1(\mathbf{r}, t) + (\partial\epsilon/\partial C_2)_0\delta C_2(\mathbf{r}, t), \quad (1)$$

where δC_1 and δC_2 are regarded as independent composition fluctuations.[4] Alternatively, one can adopt the progress variable point of view.[1,2] In Ref. 3, $(\partial\epsilon/\partial C_1)_0$ and $(\partial\epsilon/\partial C_2)_0$ were incorrectly related. In general any relationship between these derivatives must depend upon the polarizabilities of S_1 and S_2. Accordingly, Eq. (1) must be expressed as

$$\begin{aligned}\langle\delta\bar{\epsilon}(\mathbf{k}, \omega)\delta\epsilon(-\mathbf{k}, 0)\rangle = {} & (\partial\epsilon/\partial C_1)_0{}^2\langle\delta\bar{C}_1(\mathbf{k}, \omega)\delta C_1(-\mathbf{k}, 0)\rangle \\ & + (\partial\epsilon/\partial C_1)_0(\partial\epsilon/\partial C_2)_0\{\langle\delta\bar{C}_1(\mathbf{k}, \omega)\delta C_2(-\mathbf{k}, 0)\rangle \\ & + \langle\delta\bar{C}_2(\mathbf{k}, \omega)\delta C_1(-\mathbf{k}, 0)\rangle\} \\ & + (\partial\epsilon/\partial C_2)_0{}^2\langle\delta\bar{C}_2(\mathbf{k}, \omega)\delta C_2(-\mathbf{k}, 0)\rangle. \quad (2)\end{aligned}$$

The time dependence of the composition fluctuations is computed from hydrodynamics as in Ref. 3. The results are[5]

$$\delta\bar{C}_1(\mathbf{k}, \omega) = (1/\Delta)\{[+i\omega + k^2D_2 + k_b]\delta C_1(\mathbf{k}, 0) + k_b\delta C_2(\mathbf{k}, 0)\}, \quad (3)$$

and

$$\delta\bar{C}_2(\mathbf{k}, \omega) = (1/\Delta)\{[+i\omega + k^2D_1 + k_f]\delta C_2(\mathbf{k}, 0) + k_f\delta C_1(\mathbf{k}, 0)\}, \quad (4)$$

where

$$\Delta = [-\omega^2 + (\gamma_+ + 2k^2D_+)i\omega + (\gamma_+D_+{}^{-}\gamma_-D_-)k^2 + (D_+{}^2 - D_-{}^2)k^4]. \quad (5)$$

Therefore, $i(\mathbf{k}, \omega)$ will depend upon the equilibrium averages

$$\alpha_1 = \langle\delta C_1(\mathbf{k}, 0)\delta C_1(-\mathbf{k}, 0)\rangle,$$

$$\alpha_2 = \langle\delta C_2(\mathbf{k}, 0)\delta C_2(-\mathbf{k}, 0)\rangle,$$

and cross terms of the form $\beta = \langle\delta C_1(\mathbf{k}, 0)\delta\bar{C}_2(-\mathbf{k}, 0)\rangle$. Because the wavelength of visible light is long compared to equilibrium correlation lengths (we exclude the critical region), the above averages may be approximated by their $|\mathbf{k}|\rightarrow 0$ limits. These averages reduce to the case considered by Kirkwood and Goldberg.[6]

In the case where $D_1 \approx D_2 \approx D$, we find from Eqs. (2)–(5) that

$$\begin{aligned}i(\mathbf{k}, \omega) \propto {} & \{Dk^2/[\omega^2 + (Dk^2)^2]\}\langle\delta\epsilon(\mathbf{k}, 0)\delta\epsilon(-\mathbf{k}, 0)\rangle \\ & + [A(\mathbf{k})/\gamma^+](\{(Dk^2 + \gamma_+)/[\omega^2 + (Dk^2 + \gamma_+)^2]\} \\ & - \{Dk^2/[\omega^2 + (Dk^2)^2]\}), \quad (6)\end{aligned}$$

where

$$\begin{aligned}A(\mathbf{k}) = {} & \{[k_f\alpha_1 - k_b\beta](\partial\epsilon/\partial C_1)_0{}^2 \\ & + [\gamma_+\beta - k_f\alpha_1 - k_b\alpha_2](\partial\epsilon/\partial C_1)_0(\partial\epsilon/\partial C_2)_0 \\ & + [k_b\alpha_2 - k_f\beta](\partial\epsilon/\partial C_2)_0{}^2\}. \quad (7)\end{aligned}$$

This expression for $i(\mathbf{k}, \omega)$ replaces Eq. (3) of Ref. 3. The effect of the chemical reaction on the spectrum is given by the second term on the rhs of Eq. (6). Note that if (a) $(\partial\epsilon/\partial C_1)_0$ happens to equal $(\partial\epsilon/\partial C_2)_0$ or if (b) $k_f = k_b = 0$, the second term in Eq. (6) is zero. Under either of these circumstances, the entire contribution to $i(\mathbf{k}, \omega)$ arises from the diffusion broadening expressed by the first term on the rhs of Eq. (6).

In cases of physical interest, the polarizabilities of S_1 and S_2 will be different, i.e., $(\partial\epsilon/\partial C_1)_0 \neq (\partial\epsilon/\partial C_2)_0$.

If the light scattering experiment is performed under conditions where $\gamma_+ \gg Dk^2$,(1) then the major contribution to the linewidth of the central, Rayleigh line will be due to the chemical reaction.[7]

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[*] Alfred P. Sloan Research Fellow.

[†] American Can Company Predoctoral Fellow.

[1] R. D. Mountain, J. Res. Natl. Bur. Std. **A72,** 95 (1968)

[2] L. Blum and Z. W. Salzburg, J. Chem. Phys. **48,** 2292 (1968).

[3] B. J. Berne and H. L. Frisch, J. Chem. Phys. **47,** 3675 (1967).

[4] J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

[5] Note that we are ignoring cross diffusion, viscous, and thermal conduction terms in these simplified hydrodynamic equation.

[6] J. G. Kirkwood and R. J. Goldberg, J. Chem. Phys. **18,** 54 (1950). See also, J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **19,** 774 (1951).

[7] A rough estimate of $[\langle(\delta\epsilon)^2\rangle(A/\gamma_+)]$ is given by $\frac{1}{2}[(m_1-m_2)^2/(m_1^2+m_2^2)]$, where we assume $k_f=k_b$; $\langle(\delta C_1)^2\rangle\approx(\delta C_2)^2\rangle$ and the solution is ideal. The quantities m_1 and m_2 are the differences between the polarizability of species S_1 and S_2 and the inert solvent.

Exchange Energy of the Electrons in the Ar Atom and K$^+$ Ion

P. Gombás
Physical Institute of the University for Technical Sciences, Budapest, Hungary
AND
L. Porro
Gruppo Chimica Teorica, CNR, Roma, and *Instituto di Fisica Teorica della Università, Napoli, Italy*

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The total exchange energy of the Ar atom and K$^+$ ion has been calculated with the statistical exchange potential without correction and with a correction introduced by Gombás. The results show that the correction leads to a higher value of the total exchange energy of about 3‰ only, whereas it is of great importance for the energy of the exchange interaction of the valence electrons with the core electrons.

The total exchange energy E_a of an atom can be calculated approximately by the statistical model of the atom. With the help of the average exchange potential $V_a{}^m$ of Slater[1] we get

$$E_a=-\tfrac{1}{2}e\int V_a{}^m\rho dv, \tag{1}$$

where e is the positive elementary charge, ρ the electron density, and dv the volume element; the average exchange potential has the following form:

$$V_a{}^m=\tfrac{3}{2}(3/\pi)^{1/3}e\rho^{1/3}. \tag{2}$$

Last year one of us showed[2,3] that this potential cannot be used in the outer parts of the atom and has to be replaced by the following corrected form of this potential:

$$V_{a\text{ corr}}{}^m=\tfrac{3}{2}(3/\pi)^{1/3}e\rho^{1/3}[1-s_m(\tau)], \tag{3}$$

where $s_m(\tau)$ is a correction, which we can write in a good approximation in the following simple form:

$$s_m(\tau)=\tau^3=\rho_0/\rho, \qquad \tau=(\rho_0/\rho)^{1/3}, \tag{4}$$

where ρ_0 is the electron density on the boundary of the statistical Thomas–Fermi–Dirac atom

$$\rho_0=0.002127(1/a_0{}^3) \tag{5}$$

and a_0 is the first Bohr radius of the H atom.

Expression (3) is valid in the region, where $\rho\geqq\rho_0$; in the outer parts of the atom, where $\rho<\rho_0$, we have to put $V_{a\text{ corr}}{}^m\equiv0$. When we use $V_{a\text{ corr}}{}^m$ in (1), the integration has to be carried out only in that region where $\rho\geqq\rho_0$.

In this way we have calculated with uncorrected and corrected exchange potentials the total exchange energy of the electrons in the Ar atom and K$^+$ ion with the electron distributions of Hartree–Fock.[4] We got for Ar

$$E_{a\text{ corr}}=-\tfrac{1}{2}e\int V_{a\text{ corr}}{}^m\rho dv=-28.50(e^2/a_0)$$
$$=-776.1\text{ eV}, \tag{6}$$

$$E_a=-\tfrac{1}{2}e\int V_a{}^m\rho dv=-28.59(e^2/a_0)$$
$$=-778.5\text{ eV}, \tag{7}$$

$$E_a-E_{a\text{ corr}}=-0.09(e^2/a_0)=-2.4\text{ eV}; \tag{8}$$

and for K$^+$

$$E_{a\text{ corr}}=-29.69(e^2/a_0)=-808.5\text{ eV}, \tag{9}$$

$$E_a=-29.76(e^2/a_0)=-810.4\text{ eV}, \tag{10}$$

$$E_a-E_{a\text{ corr}}=-0.07(e^2/a_0)=-1.9\text{ eV}. \tag{11}$$

It can be seen that the correction has only a small influence on the total exchange energy of the atom or ion.

The case is quite different, when we introduce the correction of the exchange potential describing the action of the core electrons on a valence electron. In this case the correction gives a remarkable difference compared with the uncorrected value.[2,3] For the 4s-valence electron in the K atom one gets for the exchange energy with the core electrons without correction

$$\epsilon_a=-1.52\text{ eV}$$

and with correction

$$\epsilon_{a\text{ corr}}=-0.68\text{ eV}.$$

In this case the correction leads to a much better value than the uncorrected one. The more exact value calculated as the difference of the experimental energy and the Hartree energy of the valence electron is -0.61 eV,[3] almost the same as our corrected value.