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MOLECULAR ROTATIONS AND KINETICS BY LIGHT SCATTERING*

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Molecular Raman spectra taken at high resolution with high sensitivity reveal spectral features that have not previously been observed and which can be employed to obtain quantitative information on rotational and other kinetic behavior of the molecules. Data are given for NO_2^- and CN^- molecular impurities in alkali halides to illustrate potential applications.

The very rapid and vigorous renewal of activity in the field of light-scattering spectroscopy is well documented in the proceedings of a recent international conference on light scattering.¹ Porto's² article in that volume summarizes the variety of light-scattering phenomena that have had the most general applicability to particular scientific problems. The intention of this note is to draw attention to one technique that has not been previously emphasized and which is potentially a very powerful tool for solid-state physics, molecular physics, organic chemistry, biophysics, and molecular biology.

To illustrate, consider an isolated molecule with ν Raman-active internal modes of vibration. According to the simplest theoretical considerations,³ in a reference frame fixed with respect to the molecule (to be designated by MF), the polarizability of that molecule can be expanded to first order in these modes:

$$\alpha(t)^{\text{MF}} = \alpha^0 + \sum_{\nu=1}^{\nu} \alpha^{\nu} Q^{\nu}(t) + \dots \quad (1)$$

Assuming that the orientation of the molecule changes with time, the polarizability in the laboratory frame is obtained from $\alpha(t)^{\text{MF}}$ by a unitary transformation $\mathbf{U}(t)$, $\alpha(t) = \mathbf{U}(t)\alpha^{\text{MF}}\mathbf{U}(t)^{-1}$. The spectrum of light scattered from such a tensor polarization can be expressed in terms of the correlation functions of $\alpha(t)$. Those parts of $\alpha(t)$ that originate in the α^0 term of $\alpha(t)^{\text{MF}}$ give rise to "rotational Raman scattering."² Although rotational Raman scattering can be used to study the rotational motion of anisotropic molecules, in practice the main disadvantage of using this phenomenon is that the frequency of the light scattered is only slightly shifted from that of the incident laser light. Often this makes it difficult to separate light scattered by this mechanism from parasitic elastically scattered light. A second undesirable feature is that if the scattering system contains different types of molecules, it is impossible to separate the light scattered from each type. This should be contrasted to the light scattering that can be attributed to the other terms in Eq. (1). Omitting the term originating in α^0 , the part of the scattered-light spectrum originating in the second term in Eq. (1) is expressed in terms of fourth-rank tensors⁴

$$I_{k,j,i,j}(\omega) = (2\pi)^{-1} \int dt \exp(i\omega t) \langle [\mathbf{U}(t)\alpha^{\nu}\mathbf{U}(t)^{-1}]_{i,j} [\mathbf{U}(0)\alpha^{\nu}\mathbf{U}(0)^{-1}]_{k,j} \rangle \langle Q^{\nu}(t)Q^{\nu} \rangle. \quad (2)$$

Assuming that the internal modes are well approximated by independent simple harmonic oscillators, we can take $\langle Q^\nu(t)Q^\nu \rangle \approx \delta_{\nu,\nu} \langle (Q^\nu)^2 \rangle \cos \omega_\nu t$, where ω_ν is the eigenfrequency of the ν th Raman-active mode. For convenience, we have assumed that each mode, $\nu = 1, 2, \dots, r$, is nondegenerate. Then we have

$$I_{k,I; i,j}(\omega) = \sum_\nu (I_{k,I; i,j}^\nu + I_{k,I; i,j}^{\bar{\nu}}),$$

where

$$I_{k,I; i,j}^{\pm\nu}(\omega) = (2\pi)^{-1} \langle (Q^\nu)^2 \int dt \exp[i(\omega \mp \omega_\nu)t] \langle [U(t)\alpha^\nu U(t)^{-1}]_{i,j} [U(0)\alpha^\nu U(0)^{-1}]_{k,I} \rangle. \quad (3)$$

Although Eq. (3) can be expressed quantum mechanically, by replacing the $U(t)$ with appropriate functions of Eulerian angles, we will not present those expressions here. Note that the light-scattering spectrum described by Eq. (3) has much in common with the above-mentioned rotational Raman effect. The differences, however, are responsible for the great importance of the phenomena to which we are addressing ourselves here.

For example, the expressions for the spectrum of the rotational Raman effect involve almost the same $\langle U(\alpha)\alpha^\nu U(t)^{-1}U(0)\alpha^\nu U(0)^{-1} \rangle$ as appears here. Typically these terms are relatively slowly varying and shift the scattered light by at most 10-30 cm^{-1} from the laser light. In Eq. (3), however, we have the extra factor $\exp(-i\omega_\nu t)$ and since the ω_ν are often 1000-2000 cm^{-1} , the scattered light is well away in frequency from the incident laser light. Also each molecule has its own set of eigenfrequencies so that in a system containing different types of molecules, the light scattered from each will be at a different frequency and thus easily distinguished. The most essential point, however, as we will show below for some explicit examples, is that a great number of the most important molecules have high-frequency eigenmodes that do not couple efficiently to the nuclear or electronic excitations of the medium surrounding the molecule. This is true for many cases of molecules in either organic or inorganic, crystalline or amorphous solids and liquids as well as in gases. The effect of this is that the above description, which was presented as for an isolated molecule, is directly applicable to impurity molecules in dense host media. The only effects of the surrounding media are slight shifts in the resonance frequencies (which are not important) and major influences on the angular or orientational motion. As one can see from Eq. (3), the spectrum of the scattered light is a direct measure of this angular motion. As a practical matter, it has been possible to study impurity molecules in concentrations as low as 0.1% by this method. It is not clear that this is a true lower bound on the concentrations that can practically be studied.

Equations (2) and (3) can also describe the spectra of light scattered from the host molecules in a liquid⁵⁻⁷ or a solid. Although the rotational motions of nearby identical molecules of the host are highly correlated, the internal vibronic modes of these respective molecules are not necessarily coupled to each other. Thus the expectation value $\langle Q_1^\nu Q_2^\nu \rangle = 0$, where Q_1^ν refers to the ν th mode of molecule 1 and Q_2^ν to the ν th mode of molecule 2. In the rotational Raman effect² [i.e., originating from the α^0 term in Eq. (1)] there can be constructive or destructive interference in the light scattered from adjacent molecules implying that the scattering really measures some collective type of rotational motion. If, however, $\langle Q_1^\nu Q_2^\nu \rangle = 0$, these interference effects are absent in the effect we are discussing and the scattering spectra more nearly describe the rotational motion of individual molecules.

The data we will present in order to illustrate these spectral properties are for molecules located at sites which, in the absence of the molecule, have O_h point group symmetry. Although there are general theorems, based on group-theoretical considerations, that can be given for sites of lower symmetry we will defer discussion of these to a separate publication. Any second-rank tensor α^ν (in the molecular frame) can be written as $\alpha^\nu = 3^{-1}(\text{Tr}\alpha^\nu)\mathbf{1} + \beta^\nu$, where $\text{Tr}\beta^\nu = 0$, and $\mathbf{1}$ is the identity matrix. Since $U(t)\alpha^\nu U(t)^{-1} = 3^{-1}(\text{Tr}\alpha^\nu)\mathbf{1} + U(t)\beta^\nu U(t)^{-1}$, Eq. (3) reduces to

$$I_{k,I; i,j}^\nu(\omega) = \langle (Q^\nu)^2 \rangle [3^{-1}\text{Tr}\alpha^\nu]^2 \delta_{i,j} \delta_{k,I} \delta(\omega - \omega_\nu) + \langle (Q^\nu)^2 \rangle K_{k,I; i,j}^\nu(\omega - \omega_\nu), \quad (4)$$

where

$$K_{k,I; i,j}^\nu(\bar{\omega}) = (2\pi)^{-1} \int dt \exp(i\bar{\omega}t) \langle \beta^\nu(t)_{i,j} \beta^\nu(0)_{k,I} \rangle$$

and $\beta^\nu(t) = U(t)\beta^\nu U(t)^{-1}$. In the present special case $K_{k,I; i,j}^\nu(\bar{\omega})$ is a fourth-rank tensor that reflects the O_h point-group symmetry of the site occupied by the molecule. It follows that there are at most three

linearly independent components to this fourth-rank tensor: $K_{i,i;i,i}$, $K_{i,i;j,j}$, and $K_{i,j;i,j}$ for $i \neq j$. Taking account of the definition of $K_{i,j;k,l}$ and that $\text{Tr}\beta = 0$, for O_h symmetry $K_{i,i;i,i} = -2K_{i,i;j,j}$. In O_h symmetry, for a given molecular mode of vibration, the light-scattering spectrum predicted by Eq. (4) is a sharp line centered at ω_ν , whose intensity is proportional to $[3^{-1}\text{Tr}(\alpha^\nu)]^2$, and at most two separable sideband spectra that are direct measures of the rotational motion.

Figure 1 shows recorded light-scattering spec-

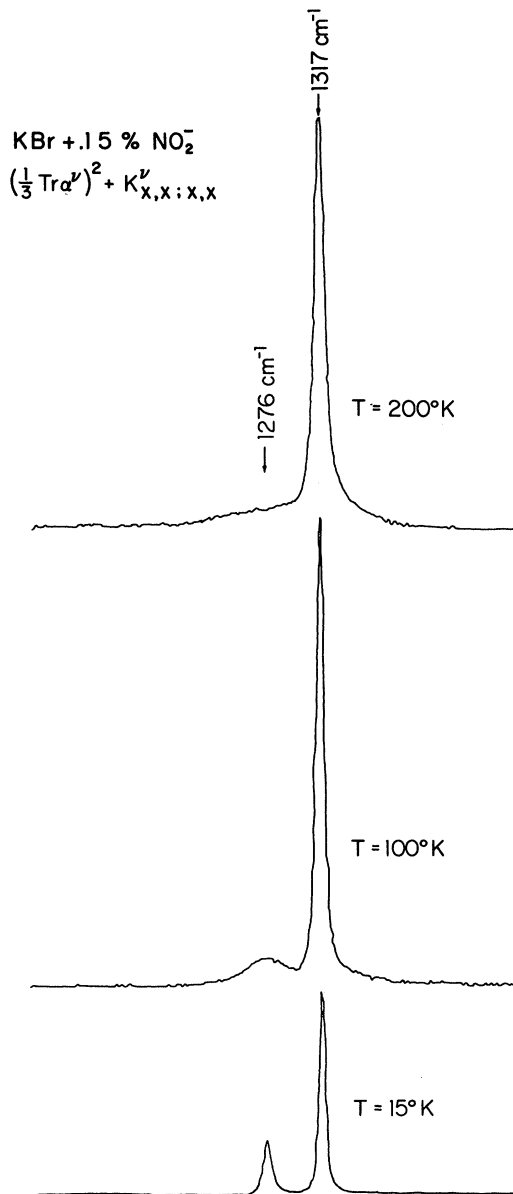


FIG. 1. Raman spectra for two internal modes of the NO_2^- impurity in KBr at three temperatures. The mode responsible for 1317-cm^{-1} line induces a diagonal polarizability tensor for which $\text{Tr}\alpha^{\text{MF}} \neq 0$. The 1276-cm^{-1} line arises from a mode for which the polarizability tensor is off-diagonal and $\text{Tr}\alpha^{\text{MF}} = 0$.

tra for the NO_2^- molecule as an impurity in KBr for three temperatures. This system has been extensively studied by infrared-absorption techniques.⁸ The isolated NO_2^- molecule has three internal modes of vibration. By symmetry considerations one can demonstrate that for two of these modes the only nonvanishing components $(\alpha^\nu)_{i,j}$ are diagonal (i.e., $i=j$) and for each of these $3^{-1}\text{Tr}(\alpha^\nu) \neq 0$. For the third mode the only nonvanishing elements $(\alpha^\nu)_{i,j}$ are for $i \neq j$ and for this mode $3^{-1}\text{Tr}\alpha^\nu = 0$. In Fig. 1 we show the spectrum of a traceless mode (1276 cm^{-1}) and one of the modes with a nonvanishing trace (1317 cm^{-1}) for three temperatures. At 300°K the NO_2^- molecule is rapidly tumbling and only the mode for which $\text{Tr}\alpha^\nu \neq 0$ is directly observed. The other mode can be seen as a broad background. However, it does not really appear distinctly until the temperature is lowered and the rotational tumbling freezes out. At the lowest temperature, the molecule is largely oriented along certain equivalent directions and both modes appear to have similar line shapes. The half-width of the 1276-cm^{-1} Lorentzian line is a direct measure of the correlation time for the NO_2^- rotational motion (i.e., 1.4×10^{-11} sec at 100°K).

The case of CN^- in KBr is a different example. This system has also been studied by a variety of other techniques.⁹ Figure 2 shows the spectrum of this example for several temperatures. In this case CN^- has only one internal mode and its α^ν has only diagonal components with $\text{Tr}(\alpha^\nu) \neq 0$. The polarizability is not isotropic since $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$. Analysis of Eq. (6) predicts a central line and two separate sideband spectra. It is possible to observe both the $K_{x,y;x,y}$ and the $K_{x,x;x,x}$ spectrum separately from the $\text{Tr}(\alpha^\nu)$ component. Because of the limited space, we show only the $K_{xx;xx}$ component. If the CN^- motion was truly isotropic rather than cubic, these two spectra would be identical. In the present example these two are similar but not identical. Figure 3 plots the separation between the peaks of the Stokes and anti-Stokes components in the $K_{x,x;x,x}$ and $K_{x,y;x,y}$ spectra versus \sqrt{T} . For freely rotating, isotropic motion, the separations of these two pairs of peaks should be equal and proportional to \sqrt{T} . In Fig. 3 the two separations are becoming equal at high temperature, but become increasingly different as the temperature is lowered. Eventually, at 70°K , the separations deviate from \sqrt{T} dependence, indicating that at these temperatures the motion is severely inhibited by the cubic (as distinct from isotropic) sym-

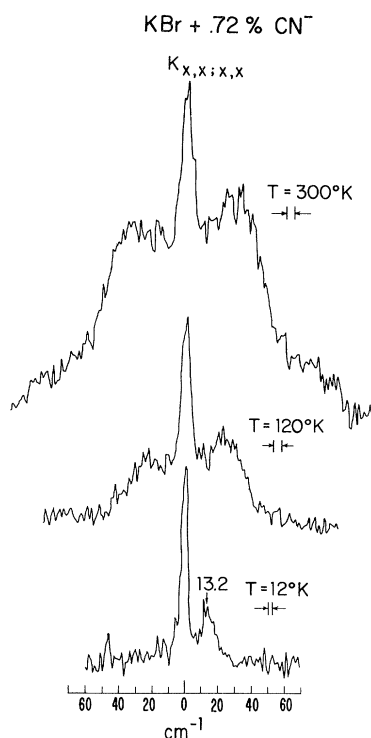


FIG. 2. Raman spectra for the $K_{x,x;x,x}(\omega)$ components of $\text{KBr}:\text{CN}^-$. Zero of the frequency scale is taken as at the eigenfrequency of the CN^- internal mode (about 2085 cm^{-1}). Positive frequency shifts to the right. The sharp central line is probably a remnant of light scattered from the $\frac{1}{3}\text{Tr}(a^{\nu})$ term. Without polarizers, the trace term would be two orders of magnitude larger than the central line shown. Although it has been substantially reduced with polarizers, it is difficult to eliminate completely.

metry of the host. At low temperatures, the Devonshire model¹⁰ can be invoked to interpret the rotational motion. This necessitates a quantum mechanical formulation of Eq. (3), which we do not present here. However, it can be shown that if the orientational wave functions of the molecule transform as various irreducible representations $\Gamma^{(i)} (=A_1, A_2, E, T_1, T_2)$ of the O subgroup of the site O_h point group, transitions between states of $\Gamma^{(i)}$ and $\Gamma^{(j)}$ symmetry will appear in the $K_{x,x;x,x}$ spectrum only if the direct product $\Gamma^{(i)} \times \Gamma^{(j)}$ contains the E representation. Similarly transitions appear in the $K_{x,y;x,y}$ spectrum only if $\Gamma^{(i)} \times \Gamma^{(j)}$ contains T_2 . These two facts are true for all modes of any arbitrary molecule. For the CN^- molecule and others, the additional symmetries of the molecule permit use of other symmetry elements contained in O_h but not contained in O . We will reserve discussion of these subtleties for a later publica-

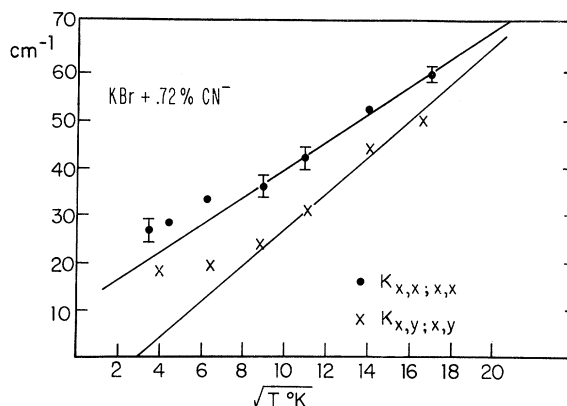


FIG. 3. The energy separation between the two peaks, Stokes and anti-Stokes, appearing on either side of the frequency for the CN^- mode (2085 cm^{-1}) for the $K_{x,x;x,x}(\omega)$ and the $K_{x,y;x,y}(\omega)$ spectra. At low temperatures, the anti-Stokes portion is frozen out and the value plotted is taken as twice the Stokes shift.

tion. Similar results have been obtained for CN^- in KBr , NaCl , NaBr , OH in KCl , and OD in KCl . Different spectra are obtained for different types of rotational motion.

The correlation functions that one studies in the phenomenon under discussion are similar to the types studied by NMR techniques. In those cases the effects of rotational motion in the hyperfine structure of proton magnetic resonance spectra yield invaluable information about molecular processes in liquids and solids. The light-scattering effects we discuss here can yield the same type of information on systems which do not have characteristic magnetic resonance signals. This technique can also be employed where NMR is inconvenient. Most important, however, light scattering is sensitive to time scales as short as 10^{-12} sec. This is many orders of magnitude outside the usable range for NMR studies. Note also that often in large organic molecules a particular ligand (like CH_3 , for example¹¹) have characteristic frequencies that are only slightly affected by the binding to the rest of the molecule. Raman scattering due to different ligands can yield information on the relative motions of different parts of the same molecule. An exciting possible application of this technique is to the study of liquid-crystal systems. Previous measurements,¹² which we are continuing in our laboratory, indicate that there are a number of sharp lines in the Raman spectrum of the nematic liquid crystal *p*-azoxyanisole that can be used to study the kinetics of the solid, mesomorphic, and liquid phases of this system.

We would like to express appreciation to Professor R. Pohl and Dr. V. Narayanamurti for stimulating discussions concerning basic physical properties of several systems studied, and also to Dr. R. Meyer for many helpful discussions on liquid crystals.

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¹Light Scattering Spectra of Solids, edited by G. B. Wright (Springer-Verlag, Berlin, Germany, 1969).

²S. P. S. Porto, in Ref. 1, p. 1.

³G. Placzek, in *Handbuch der Radiologie*, edited by E. Marx (Akademie Verlagsgesellschaft, Leipzig, Germany, 1934), Vol. 6, Pt. 2, p. 209. Some aspects of rotational Raman scattering appear in many of these early papers. In view of the available experimental tools at that time, these ideas were not fully pursued.

⁴See, for example, A. A. Maradudin, *Solid State Phys.* **19**, 1 (1966). In particular, the notation is defined by Eqs. (4.1) and (4.3) of this reference. The re-

lationship between the experimental polarizations and these tensors is explained in this reference.

⁵The observed spectra from benzene [M. McClintock, D. A. Jennings, and M. Mizushima, *Phys. Rev. Letters* **21**, 276 (1968)] can be understood in terms of this analysis. Also some of these same ideas have previously been considered theoretically for homogeneous isotropic liquids. See, for example, R. G. Gordon, *J. Chem. Phys.* **42**, 3658 (1965), and Gordon's earlier papers; as well as papers by R. Pecora and W. A. Steele, *J. Chem. Phys.* **42**, 1872 (1965), and their earlier papers.

⁶Gordon, Ref. 5.

⁷Pecora and Steele, Ref. 5.

⁸V. Narayanamurti, W. D. Seward, and R. O. Pohl, *Phys. Rev.* **148**, 481 (1966).

⁹W. D. Seward and V. Narayanamurti, *Phys. Rev.* **148**, 463 (1966).

¹⁰A. F. Devonshire, *Proc. Roy. Soc. (London)*, Ser. A **153**, 601 (1936).

¹¹G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945). See, for example, Table 85 and Fig. 92 on p. 315; also various other portions of Sec. III, 3, pp. 271-369.

¹²H. Froymann and R. Servant, *Ann. Phys. (Paris)* **20**, 131 (1945).

LEVEL CROSSING IN CH₄ OBSERVED BY NONLINEAR ABSORPTION

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Stark-tuned level crossing resonances in an excited vibration-rotation state of methane were detected through nonlinear optical absorption. The signal accurately follows a Lorentzian line shape with a 200-kHz minimum width. Pressure broadening studies yield the rotational relaxation in the excited vibrational state.

Nonlinear optical techniques have recently been reported which produce unusually high-resolution spectra in Doppler-broadened transitions. These nonlinear methods include level crossing, mode crossing, and Lamb-dip effects and have been restricted to atomic laser systems such as Xe,^{1,2} O,³ and Ne.⁴⁻⁶ Presently, these methods are being extended to molecules where Lamb-dip resonances have been observed in CH₄,⁷ I₂,⁸ and NH₂D.⁹ In the last case, precision Stark spectroscopy in the infrared was demonstrated.

We report here the first observation of molecular level crossing by saturated absorption. Methane in the vibrationally excited ν_3 mode is examined. This excited state possesses a small dipole moment, exhibits a weak first-order Stark effect, and allows observation of a Stark-tuned level-crossing signal about zero field. The sig-

nal is monitored by nonlinear absorption from the ground state with a magnetically tuned 3.39- μ He-Ne laser. The observed line shape reflects only the excited-state inverse lifetime of the crossing levels and accurately obeys a Lorentzian function with a half-width which is linearly dependent on pressure and which can be as narrow as 200 kHz. By comparison, the (inverted) Lamb-dip widths recently reported for CH₄⁷ are nearly identical to these results. Since Lamb-dip widths reflect an average of both ground- and excited-state inverse lifetimes, we conclude that rotational relaxation in the ground and excited vibrational states is nearly the same.

A few molecular zero-field level crossings have also been observed in spontaneous emission by the conventional Hanle arrangement.¹⁰⁻¹² However, these signals are weak because of the com-