

correspond to a weaker dependence of plasma frequency on wave number than that given here; such real metal effects could modify our conclusions concerning the resonant peaks, but we have adopted a free-electron model because of its analytical simplicity and utility as an example.

In conclusion we wish to point out that Eqs. (3) are quite general and apply to any system possessing longitudinal electric polarization waves which are noninteracting with the transverse electromagnetic waves. Thus, for example, they may be applied to a polar crystal such as an alkali halide which possesses a longitudinal optic mode.

*Research supported by National Science Foundation Grant No. GP 5098. This work represents a portion of a thesis submitted by A. R. M. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Michigan State University.

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ANGULAR-CORRELATION FUNCTIONS OF DIATOMIC ROTATORS IN ALKALI HALIDES

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(Received 17 May 1968)

For the first time, angular-correlation functions of diatomic rotators in solids have been determined experimentally using vibration-rotation spectra. As samples we used OH^- and OD^- in KCl . Maxima and minima of the correlation function show an isotopic shift.

Random rotation or tumbling of diatomic molecules in gases, liquids, or solids represents a stationary process.¹ In accordance with the theorem² of Wiener and Khintchin, the angular autocorrelation function can therefore be calculated as the Fourier transform of the normalized absorption observed in the rotation spectrum or the vibration-rotation spectrum. For the vibration-rotation spectrum, the angular autocorrelation function is given by

$$\int_0^\infty I(\omega) \cos \omega t d\omega \cong \langle \vec{u}(0) \vec{u}(t) \rangle \cos(\omega_0 t) \\ = 3 \langle \cos \theta(0) \cos \theta(t) \rangle \cos \omega_0 t,$$

where $I(\omega)$ indicates the normalized absorption, ω_0 the frequency corresponding to the vibrational transition, and

$$\vec{u}(t) = [\sin \theta(t) \cos \varphi(t), \sin \theta(t) \sin \varphi(t), \cos \theta(t)]$$

the unit vector in the direction of the oscillating electric dipole. This equation has been derived by Gordon³ and Brot⁴ for liquids and gases. The

correlation functions evaluated from our spectra of HCl and HBr in CCl_4 are in good agreement with those of CO in CCl_4 , C_6H_{14} , etc., determined by Gordon³ from spectra of Josien and Bulanin.⁵

The rotation or tumbling of OH^- and OD^- in alkali halides has been observed by dielectric relaxation,⁶ and ultraviolet and infrared spectroscopy.⁷ All measurements indicate a strong influence of a cubic crystal-field potential acting on the diatomic molecule as described by Devonshire⁸ and Sauer.⁹ Therefore we expected to find a special behavior of the angular-correlation functions of diatomic rotators in crystal fields. We have measured the vibration-rotation spectra on OH^- and OD^- in KCl near 3700 and 2700 cm^{-1} at room temperature. The corresponding autocorrelation functions, superposed by the vibrational decay function, are shown in Fig. 1. Group-theoretical considerations demonstrate the applicability of the above correlation functions for rotators in liquids and in local fields of cubic symmetry.¹⁰ For short times ($t < 0.5 \times 10^{-13}$ sec) the

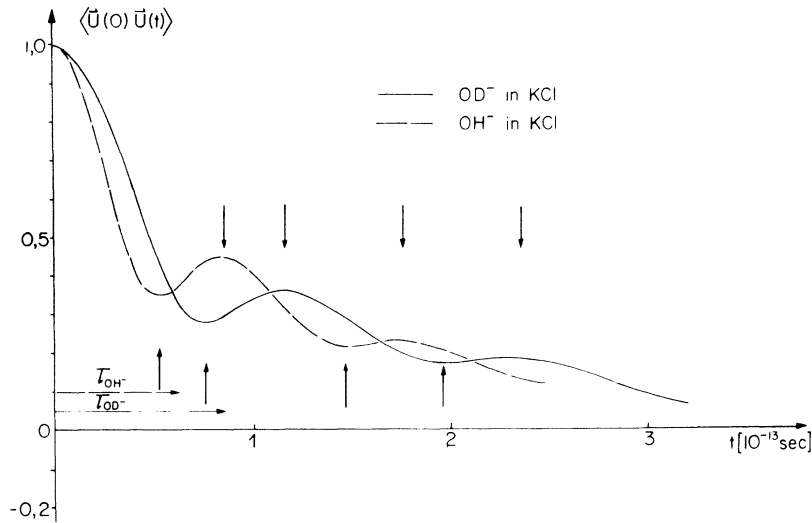


FIG. 1. Angular autocorrelation functions of OH^- and OD^- in KCl determined from the vibration-rotation spectra measured at room temperature.

correlation function can be approximated by

$$\langle \vec{u}(0) \cdot \vec{u}(t) \rangle = 1 - (I/kT)t^2 + \text{higher terms},$$

with I the moment of inertia and T the absolute temperature. In this approximation the correlation function is entirely defined by the statistics of the angular momentum and not yet influenced by collisions. For long times ($t > 5 \times 10^{-13}$ sec), the correlation functions approach the exponential decay observed in magnetic resonances and characteristic for Markoff processes.^{3,11-13} In

the transition range between 5×10^{-13} and 0.5×10^{-13} sec the correlation function depends strongly on the interaction of the rotator with its vicinity. Here the correlation functions of rotators in gases, liquids, and crystals differ considerably.^{4,11,14,15} The most remarkable features of the correlation functions of Fig. 1 are the maxima and minima present in the transition region. The time differences corresponding to these maxima and minima show an isotopic shift for OH^- and OD^- . They are proportional to the square roots of the moments of inertia, as shown in the following table:

$t_{\text{extr-extr}}$ (10^{-13} sec)			Moment of inertia (Ref. 16) (10^{-40} cgs)	
OH^-	OD^-	Ratio	OH^-	OD^-
0.850	1.17	1.37	1.53	2.91
0.875	1.15	1.32	(ratio) ^{1/2} = 1.37	
0.945	1.22	1.29		

For comparison, the rotational time constants $\tau = (I/kT)^{1/2}$ based on the moments quoted in the literature¹⁶ are marked in Fig. 1. Theory^{8,9,17} and experiment^{6,7} support the assumption that the potential minima for the rotator lie in the (100) and the maxima in the (111) directions. Infrared-absorption measurements by Chau, Klein, and Wedding¹⁸ suggest a librational motion of the ions OH^- and OD^- in the host crystal. If we assume the time differences between the maxima to correspond to the half-periods of the librations, we find the following average libration frequencies

at room temperature:

for OH^- , 381 cm^{-1} ; for OD^- , 287 cm^{-1} .

The frequencies reported by Chau, Klein, and Wedding for 4.6°K were 293 and 225 cm^{-1} , respectively. However, we cannot yet decide about an eventual contribution of quasifree rotations to the correlation functions, but we intend to solve this problem by variation of temperature.¹⁹

We hope that the angular-correlation functions of diatomic rotators obtained from vibration-ro-

tation spectra will provide more valuable information on librations and hindered rotations.

We wish to thank Professor W. Känzig and his group for helpful discussions and for growing the crystals.

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DYNAMICS OF EXCITED-STATE ANNIHILATION IN NdCl₃

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(Received 21 May 1968)

Two processes are observed in NdCl₃ whereby two excited Nd³⁺ ions undergo a transition leaving one ion in a higher excited state and the other in a lower state. In one case the initial states are the same, namely ⁴F_{3/2}; in the other they are different, ⁴F_{3/2} and ⁴I_{15/2}. In both cases fluorescence decays of initial and final states are measured, allowing the determination of the rate equation for the processes.

A number of recent papers¹⁻⁶ have been concerned with processes whereby two ions in excited states annihilate, leaving one of the ions in a higher excited state and the other in a lower state. The evidence for such processes is the emission of light from single-ion excited states at energies much more than kT greater than the excitation energy, or the generation of free charge carriers. When the efficiency of the process is relatively high, a change is observed in the decay of the states involved.^{5,7} The emission from higher excited states can also result from simultaneous and sequential two-photon absorption of the excitation by single ions.⁸ It is necessary to perform fluorescence decay studies or to carry out careful wavelength determinations² in order to ascertain which of the processes is important.

This Letter reports determination of the rate

equations for two processes of Nd³⁺ in NdCl₃, one in which an ion in W annihilates with an ion in R and another in which two ions in R annihilate. The energy levels⁹⁻¹² of Nd³⁺ and their spectroscopic notation are shown in Fig. 1.

I. The rate equations.— The lowest order rate equations which can describe excited-state annihilation are given, for pulsed excitation, by

$$\frac{dN_1}{dt} = -\frac{N_1}{\tau_1} - \gamma_{12}N_1N_2 + \gamma_{34}N_3N_4, \quad (1)$$

$$\frac{dN_2}{dt} = -\frac{N_2}{\tau_2} - \gamma_{21}N_2N_1 + \gamma_{34}N_3N_4, \quad (2)$$

$$\frac{dN_3}{dt} = -\frac{N_3}{\tau_3} + \gamma_{12}N_1N_2 - \gamma_{34}N_3N_4, \quad (3)$$

$$\frac{dN_4}{dt} = -\frac{N_4}{\tau_4} + \gamma_{12}N_1N_2 - \gamma_{34}N_3N_4; \quad (4)$$