

Collision-Induced Absorption of Hydrogen Deuteride Dissolved in Liquid Neon

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First observation of the collision-induced IR-fundamental band of hydrogen deuteride (HD) in liquid neon is described. A developed intracell rattling model yields highly accurate fits to the measured diffuse Q_1 -branch profiles enabling a detailed shape analysis of the adjacent spectral lines. Strong intracollisional anticorrelation found at the location of the permanent dipole-allowed $R_1(0)$ transition is interpreted in the frame of the Fano-Mori theory. A new striking narrowing effect (by 30%) is observed on the sharp $Q_1^q(0)$ vibrational line with increasing HD concentration in solutions. The $T_1(0)$, $U_1(0)$ and a few pair transitions are identified in the spectrum.

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Interaction-induced vibration-rotation-translation spectra of molecular hydrogen furnish a unique opportunity to study translational motion and its coupling to the internal degrees of freedom of molecules in high-density phases [1,2]. Further unusual effects appear in the spectra of hydrogen deuteride (HD) because the center of mass in this molecule is shifted from the bond midpoint. This results in an extra torque exerted on the HD molecule from neighboring particles that makes its rotation stronger perturbed compared to symmetric H_2 and D_2 and reveals more detail on the molecular motion dynamics in condensed media. The lack of the center-of-mass inversion symmetry for HD renders active the rotational transitions with $\Delta J = \text{odd}$ [3]. Because of the intramolecular electronic-rotovibrational coupling, HD acquires a small permanent dipole moment M_a , comparable in magnitude with the typical values of the collision-induced dipole moments μ_{ab} . The intracollisional correlation (IC) between these dipoles distorts the allowed P_1 and R_1 spectral line profiles [4] mostly studied so far in the gas-phase spectra (see, e.g., [5,6], and references therein). Similar effects were observed in the liquid state (neat HD [7] and its solution in Ar [3]), but no theoretical interpretation was advanced.

We report here new data on the structure of the previously unexplored fundamental absorption band of HD dissolved in liquid neon at different temperatures and concentrations. By varying the HD concentration x_{HD} in solution one can identify spectral features induced by the guest-host and guest-guest interactions, the latter being responsible for the appearance of the so-called simultaneous transitions (ST) resulting in excitation of a pair of interacting HD molecules by a single photon. The excited rotational states become depopulated at low temperatures of our experiments, which simplifies the spectral band structure and favors resolution of finer details. On the other hand, the Ne solvent density changes in the temperature range covered are large enough [8] to significantly modify both the frequency distribution and the integrated band intensity.

A remarkable narrowing of the $Q_1^q(0)$, $\Delta J = 0$ vibrational spectral line was found upon increase of the solute concentration in solution; to the best of our knowledge, no such self-induced line narrowing effect was observed before. To separate this and the permanent dipole-allowed $R_1(0)$ spectral features from the diffuse collision-induced Q_1 -branch background, the background shape is fitted using a simple cage model of liquid. A general Fano-Mori approach to the IC shape theory is outlined.

The spectra were recorded at 0.5 cm^{-1} resolution with a Bruker IFS 66v FTIR interferometer in combination with a Ge/KBr beam splitter, a Globar source, and a broadband MCT detector, by averaging 1000 scans and applying the Blackman-Harris apodization. Gas samples of HD (Isotec, stated purity 98%) and Ne (Air Liquide, stated purity 99.995%) were used without further purification. Premixed gases were condensed in a sample cell attached to the cold head of a Leybold ROK 10-300 double stage cryostat. The cell of 4 cm pathlength, made of brass and designed to withstand internal pressure of at least 30 bar, was equipped with a pair of 1° -wedged silicon windows sealed by indium gaskets and with two Si diodes located at the top and the bottom of the cell body for temperature control in the range of 24–43 K. The setup did not allow us to control whether all HD from the gas mixtures was actually dissolved in liquid neon, so that no measurements of the absolute spectral intensities were attempted. The nominal x_{HD} values were in the 0.01–0.04 mole fraction (m.f.) range.

Spectral assignment.—Some of the recorded spectra are shown in Figs. 1 and 2. A surprisingly sharp $Q_1^q(0)$ feature appears at the pure vibration frequency $\nu_0 = \omega_0/2\pi c = 3632.1 \text{ cm}^{-1}$ (all quoted free-molecule frequencies are taken from Ref. [9]). A prominent asymmetric dip is located at the position of the allowed $R_1(0)$ line at $\nu = 3717.5 \text{ cm}^{-1}$. At higher temperatures, a similar dip develops near the $P_1(1)$ line, at $\nu = 3542.9 \text{ cm}^{-1}$, and a weak absorption peak due to the $R_1(1)$ transition, $\nu = 3798.4 \text{ cm}^{-1}$, becomes visible on the slope of the broad Q_1^q band. The unresolved doublet band near

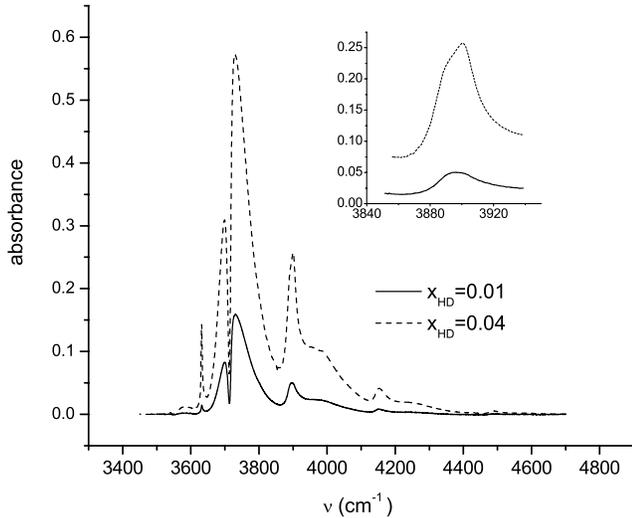


FIG. 1. HD fundamental absorption band at $T = 25.7$ K at two different HD concentrations. The inset shows the enlarged part of the spectrum near the $S_1(0)$ transition.

3900 cm^{-1} observed at $x_{\text{HD}} = 0.04$ m.f. is formed by the induced $S_1(0)$ single transition at 3887.6 cm^{-1} and overlapping ST $Q_1(0) + S_0(0)$, $\nu = 3899.2\text{ cm}^{-1}$, that becomes undetectable in the spectrum of a more dilute solution. A broad shoulder near 4000 cm^{-1} is most likely the S_1^r intracell rattling component. Next are the $\Delta J = 3$ [$T_1(0)$ line at 4141.3 cm^{-1}] and $\Delta J = 4$ [$U_1(0)$ line at 4476.7 cm^{-1}] transitions. Their blue wings overlap with the positions of the $S_1(0) + S_0(0)$ ($\nu = 4154.3\text{ cm}^{-1}$), $Q_1(0) + T_0(0)$ ($\nu = 4164.5\text{ cm}^{-1}$) and $Q_1(0) + U_0(0)$ ($\nu = 4515.4\text{ cm}^{-1}$) lines. However, no concentration effects on the blue wing distributions were detected and, hence, these STs have negligible intensities. Except $Q_1(0) + S_0(0)$, the only ST observable feature is $S_1(0) + T_0(0)$, $\nu = 4419.6\text{ cm}^{-1}$ which becomes visible in the $x_{\text{HD}} = 0.04$ m.f. solution. It rapidly fades away with increasing temperature (see inset to Fig. 2). To make the absorbances on the inset approximately equal, they were rescaled by normalizing the spectra by the unity area.

Separation of components near the band origin.— The spectral density function $W(\omega)$ is obtained from the measured absorbance $A(\omega)$ by $W(\omega) = (\omega_0/\omega)[1 - \exp(-\hbar\omega/kT)]A(\omega)$. Within the experimental uncertainty, the Boltzmann relation $W(-\Delta\omega) = W(\Delta\omega)\exp(-\hbar\Delta\omega/kT)$ holds relative to the band origin, i.e., by taking $\Delta\omega = \omega - \omega_0$. This implies that the translational motion of solutes remains decoupled from molecular vibrations and, possibly, from rotations as well, as suggested by the quantum asymmetry apparent on the partially resolved $T_1(0)$ and $U_1(0)$ spectral profiles (see Figs. 1 and 2).

We assume HD solutes to make one-dimensional oscillations with the frequency ω_r between the cage walls formed by the Ne atoms. Since the intensity of the diffuse part of the Q branch originates from the short-range

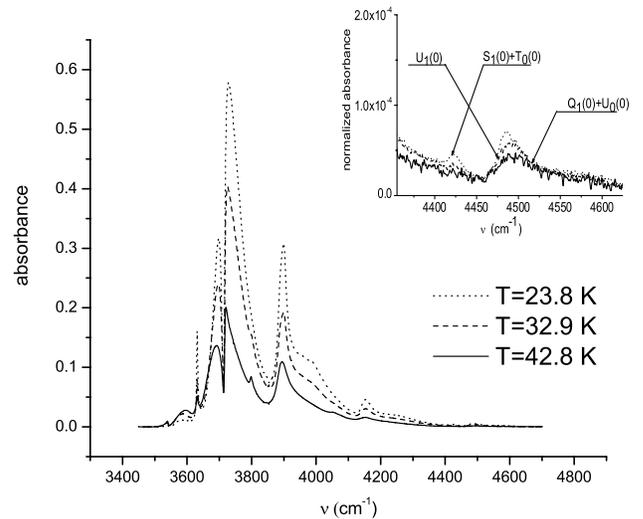


FIG. 2. Fundamental band of HD in liquid neon at $x_{\text{HD}} = 0.04$ m.f. Inset: $U_1(0)$ spectral feature; arrows indicate the transition frequencies.

terms of the induced dipole moment function, one may expect the HD molecule to effectively interact with a single Ne atom during impact with the wall. In that case, the impact time correlation function $C_0(t)$ will have the same form as for the isolated gas-phase binary collisions with the mean duration $t_c = \omega_c^{-1}$. Finally, intracell rattling and wall collisions are considered as statistically independent events, which yields the shape function $W_s(\Delta\omega) = [W_0(\Delta\omega + \omega_r) + W_0(\Delta\omega - \omega_r)]/2$, where $W_0(x)$ is the Fourier transform of $C_0(t)$. The model function we are using is $W_0(x) = A\exp(\lambda - [\lambda^2 + (x/\omega_c)^2]^{1/2})$, previously shown [10] to accurately fit the shapes of the translational absorption in rare-gas mixtures, also induced by the short-range interactions [11]. The λ parameter is temperature insensitive, so a fixed value of $\lambda = 1.5$ was taken [10]. Next, a correcting factor $D(\Delta\omega) = 1 - d\exp[-(\Delta\omega/\omega_r)^2/2]$ was introduced to improve the quality of fits near ω_0 . The symmetrized four-parametric $(A, \omega_c, \omega_r, d)$ model shape function $\tilde{W}(\Delta\omega)$ then becomes

$$\begin{aligned}\tilde{W}(\Delta\omega) &\equiv [W(\Delta\omega) + W(-\Delta\omega)]/2 \\ &= W_s(\Delta\omega)D(\Delta\omega)E(\Delta\omega),\end{aligned}$$

where $E(\Delta\omega) = \cosh(\hbar\Delta\omega/2kT)$ corrects for the quantum effects.

The fittings were performed in the frequency ranges where contributions due to the $R_1(0)$ and $Q_1^q(0)$ features are negligible and produced profiles indiscernible from the experimental data. Since the shapes of the diffuse collision-induced Q branches are smooth, one may interpolate $\tilde{W}(\Delta\omega)$ to obtain the $R_1(0)$ and $Q_1^q(0)$ line profiles as differences between the measured and simulated distributions. The inverse collision time ω_c should increase

with T (classically as \sqrt{T}); indeed, the corresponding frequency factors ($\omega_c/2\pi c$) were found to increase from 21 cm^{-1} at $T = 23.8 \text{ K}$ up to 29 cm^{-1} at $T = 42.8 \text{ K}$. From the latter value one can estimate [10] the induced-dipole range parameter, $R_0 = 0.72 \text{ a.u.}$, a value consistent with the short-range nature of the dipole moment responsible for the appearance of the diffuse Q_1 -branch component. The rattling frequency ω_r depends on the cage radius a ($\omega_r \sim a^{-2}$). In turn, a depends on the solvent density ρ_b , which is strongly subjected to temperature [8]. For instance, at outer pressure of 20 atm, one gets from Ref. [8]: $\rho_b = 1416 \text{ Amagat}$ ($T = 23.8 \text{ K}$) and $\rho_b = 902 \text{ Amagat}$ ($T = 42.8 \text{ K}$). The rattling slows down as more space for HD motion becomes available, indeed $\omega_r/2\pi c$ was found to decrease from 73 cm^{-1} at $T = 23.8 \text{ K}$ to 40 cm^{-1} at $T = 42.8 \text{ K}$.

Intracollisional shape.—An unusual feature observed in the spectrum of the HD-Ne system is that the $R_1(0)$ and $P_1(1)$ transitions appear not as ordinary absorption peaks, but as asymmetric dips on the Q_1 -branch background. The dip asymmetry is enhanced with increasing temperature and a positive bump appears at the blue side of the $R_1(0)$ feature (see Fig. 3). A similar but far less developed pattern was previously observed in pure gaseous HD and its mixtures with rare gases in both pure rotational [12] and rotovibrational spectra [13].

We treat cross correlation between the permanent dipole M_a of a particular HD molecule and the net induced dipole moment $\mu^\Sigma = \sum_b \mu_{ab}$ by applying the Fano-Mori technique [14]. The molecule is characterized by a set of the allowed rotovibrational transitions $I \rightarrow F$ associated with the line-space vector $|K\rangle = \rho_{aI}^{-1/2} |IF^\times\rangle$ and the matrix elements $M_K = \sqrt{\rho_{aI}} \langle I | M_a | F \rangle$, where ρ_a is the molecular density matrix. The collision-induced dipole $\mu^\Sigma = |\mu^\Sigma(q)\rangle$ depends also on a set of the translational coordinates q . With the help of two projectors \hat{P} and $\hat{Q} =$

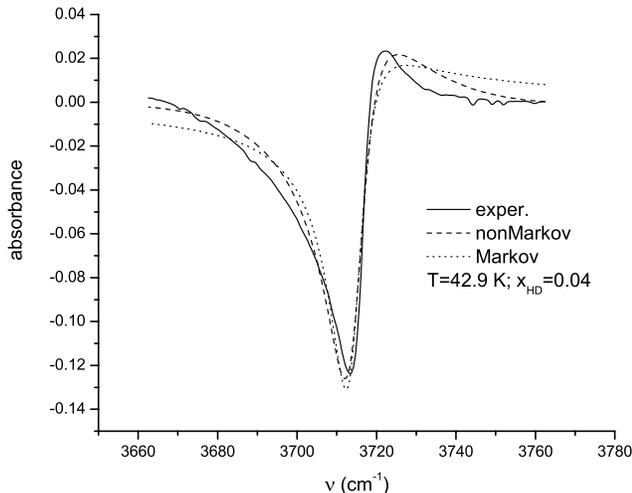


FIG. 3. Intracollisional $R_1(0)$ shape.

$1 - \hat{P}$, it can be decomposed into two orthogonal (in the sense of the line-space metric [14]) components, one ($|\mu_P\rangle$) varying in-phase with M_a , and the other ($|\mu_Q\rangle$) corresponding to the rapidly fluctuating part of the collision-induced dipole. The in-phase component when added to M_a , simply rescales line intensities in the allowed spectrum as $M_K^2(1 + f_K)^2$ via the real, density-dependent coefficients $f_K = M_K^{-1} \langle\langle K | \mu_{IF}^\Sigma \rangle\rangle$.

In our case the allowed lines are well apart from each other, so the self-part of the complex spectral function near $\omega_K = \omega_{FI}$ is given by

$$S_{\text{self}}(\omega) = \frac{i}{\pi} \frac{M_K^2(1 + f_K)^2}{\omega - \Omega_K + i\Gamma_{KK}} + S_Q(\omega),$$

where $S_Q(\omega)$ is the background spectrum associated with μ_Q . The “dressed” frequency Ω_K may differ from ω_K because of the bath-molecule coupling Liouvillian \hat{L}_1 . The complex damping parameter $\Gamma_{KK} = \Gamma'_{KK} + i\Gamma''_{KK}$ is determined by the self-spectrum of $|L_1K\rangle$ [14]. The derived cross term

$$S_{\text{cross}}(\omega) = \frac{1}{\pi} \frac{M_K^2(1 + f_K)\Phi_K}{\omega - \Omega_K + i\Gamma_{KK}},$$

contains the factor Φ_K defined by the cross-correlation spectrum of rapidly decaying fluctuations $|L_1K\rangle$ and $|\mu_Q\rangle$.

$$\Phi_K = \langle\langle K | L_1^\dagger Q \frac{i}{\omega - LQ} | \mu_Q \rangle\rangle + \langle\langle \mu_Q | Q \frac{i}{\omega - LQ} L_1 | K \rangle\rangle,$$

where \hat{L} is the total Liouvillian. For detunings from ω_K much smaller than the inverse time τ_c^{-1} of the fluctuation decay, Φ_K and Γ_K do not depend on ω . Such detunings correspond to the Markovian collisions in the gas phase.

The total absorption profile is obtained as the real part of $S_{\text{self}}(\omega) + S_{\text{cross}}(\omega)$. In the Markovian limit, it reduces to the Fano profile with an asymmetric dispersion term determined by $\Phi'_K = \text{Re } \Phi_K$. The imaginary part $\Phi''_K = \text{Im } \Phi_K$ contributes to the integrated intensity $I_K = M_K^2(1 + f_K)(1 + f_K + \Phi''_K)$, which—dependent on the values of f_K and Φ''_K —can be either positive or negative. The signs of Γ'_{KK} and Φ'_K depend on the relevant initial-time correlations: obviously, $\Gamma'_{KK}(\omega) > 0$ and the sign of $\Phi'_K(\omega)$ coincides with that of $M_K \langle\langle \mu_Q | L_1 | K \rangle\rangle$ irrespective of the frequency. The signs of Γ''_{KK} and Φ''_K cannot be easily predicted. Since μ_{IF}^Σ is given by the sum of binary contributions, f_K is proportional to the solvent density ρ_b and only small deviations from the linear dependence are possible. In the case of Φ_K and Γ_{KK} , the linear law holds only under the binary-collision regime.

Except the neglect of line mixing, the obtained results are rigorous and five independent real constants ($f_K, \Gamma'_{KK}, \Omega_K + \Gamma''_{KK}, \Phi'_K, \Phi''_K$) specify the spectral profile in the Markovian limit. However, only four

combinations p_k ($k = 1, 2, 3, 4$) of these constants can be extracted from the measurement:

$$p_1 = \frac{M_K^2(1+f_K)(1+f_K+\Phi_K'')}{\pi\Gamma_{KK}'}, \quad p_2 = \Gamma_{KK}',$$

$$p_3 = \Omega_K - \Gamma_{KK}'' - \omega_{fi}, \quad p_4 = \frac{\Phi_K'}{(1+f_K+\Phi_K'')}.$$

Furthermore, only the sign of p_1 is physically meaningful because the absolute intensities have not been measured in the present study. The gas-phase data for HD-Ne at $T = 77$ K [13] suggest negative scaling: $1+f_K < 0$. Since p_1 and p_4 remain negative at any temperature, we conclude that $\Phi_K'' + 1 + f_K > 0$, $\Phi_K' < 0$; the latter implies that $M_K \langle \langle \mu_Q | L_1 | K \rangle \rangle < 0$.

As Fig. 3 shows, the Markovian fit systematically overestimates the intensity in the $R_1(0)$ dip wings. This is caused by a too slow decay (as $|\Delta\omega|^{-1}$) of the dispersion component at large detunings. Therefore, some non-Markovian correction should be introduced first for $\Phi'(\Delta\omega)$. For instance, the use of a Gaussian function for $\Phi'(\Delta\omega)$ indeed improves the quality of the fit to the experimental profile.

The $J = 1$ solute state begins to be noticeably populated at $T = 42.8$ K and the $P_1(1)$ and $R_1(1)$ transitions become observable. Although their recorded intensities were too small for a quantitative treatment, two features can be noted. First, the $P_1(1)$ dip profile is qualitatively a reflection at the band origin of the $R_1(0)$ profile, indicating that $\Phi'_{P_1(1)} > 0$. This result suggests that the rotational contributions to $\Phi'_{P_1(1)}$ and $\Phi'_{R_1(0)}$ are dominating. These two transitions have inverted initial and final rotational quantum numbers and such inversion changes the sign of Φ'_K , in agreement with observed behavior. Second, the IC effects on the $R_1(1)$ shape are constructive and less pronounced compared to the $R_1(0)$ case, as was also observed in the spectrum of a compressed HD-Ne gas mixture at $T = 77$ K.

Vibrational $Q_1^q(0)$ line.—This sharp line must be induced by the “isotropic” part of μ_{ab} insensitive to molecular rotation. The dispersion contribution, $\mu_{ab} \sim D_7 R^{-7}$, seems to be the most likely candidate. After separation from the diffuse Q_1 -branch background, its shape appears as a Lorentzian shifted by 0.7 cm^{-1} to lower frequencies compared to the gas phase [9]. Since the solute rotation is not involved, the $Q_1^q(0)$ line half-width γ reflects the combined effect of translational and vibrational degrees of freedom. Temperature variation of γ (HWHH) is linear, increasing from $2.0(1) \text{ cm}^{-1}$ at 23.8 K to $4.4(3) \text{ cm}^{-1}$ at 42.8 K in the $x_{\text{HD}} = 0.04$ m.f. solution. These values are about 3 times smaller than the $R_1(0)$ half-width, which is dependent also on the rotational relaxation. The area under the $Q_1^q(0)$ line A ($T = 25.7$ K) increased by more than sevenfold in the spectrum

of the solution with $x_{\text{HD}} = 0.04$ m.f. compared to that observed in the $x_{\text{HD}} = 0.01$ m.f. solution. The measured values fit the equation $A(x_{\text{HD}}) = A_1 x_{\text{HD}} + A_2 x_{\text{HD}}^2$ with $A_1 = 7.5 \text{ cm}^{-1}$ and $A_2 = 320 \text{ cm}^{-1}$ showing that both HD monomers and dimers contribute in the induction of this spectral line.

The most striking observation is a strong concentration narrowing of the $Q_1^q(0)$ line. Its HWHH ($T = 25.7$ K) decreased from $3.2(1) \text{ cm}^{-1}$ at $x_{\text{HD}} = 0.01$ m.f. to $2.1(1) \text{ cm}^{-1}$ at $x_{\text{HD}} = 0.04$ m.f. Pure translational narrowing mechanism can hardly apply because HD concentrations were too small to perturb so strongly the solvent motion. One may consider the vibrational perturbations as the most probable cause, however, to explain how the combined action of dephasing and vibrational energy transfer could produce a net line narrowing remains unclear and requires further study.

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- [1] J. van Kranendonk, *Solid Hydrogen* (Plenum Press, New York, 1983).
- [2] *Molecular Cryospectroscopy*, edited by M. O. Bulanin, Advances in Spectroscopy Vol. 23, edited by R. J. H. Clark and R. E. Hester (Wiley & Sons, Chichester, 1995), Ch. 6.
- [3] G. W. Holleman and G. E. Ewing, *J. Chem. Phys.* **44**, 3121 (1966); **47**, 571 (1967).
- [4] R. M. Herman, R. H. Tipping, and J. D. Poll, *Phys. Rev. A* **20**, 2006 (1979).
- [5] M. Gustafsson and L. Frommhold, *Phys. Rev. A* **63**, 052514 (2001).
- [6] A. R. W. McKellar, *Can. J. Phys.* **64**, 227 (1986).
- [7] M. J. Clouter and A. R. W. McKellar, *Can. J. Phys.* **65**, 1 (1987).
- [8] *Handbook on Thermophysical Properties of Gases and Liquids*, edited by N. B. Vargaftik (Nauka, Moscow, 1979).
- [9] B. P. Stoicheff, *Can. J. Phys.* **35**, 730 (1957).
- [10] A. P. Kouzov, *Opt. Spektrosk.* **30**, 841 (1971).
- [11] U. Buontempo, S. Cunsolo, and G. Jacucci, *Can. J. Phys.* **49**, 2870 (1971).
- [12] A. R. W. McKellar, J. W. C. Johns, W. Majewski, and N. H. Rich, *Can. J. Phys.* **62**, 1673 (1984).
- [13] A. R. W. McKellar and N. H. Rich, *Can. J. Phys.* **62**, 1665 (1984).
- [14] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Benjamin, Massachusetts, 1975).