

## Instantaneous Normal Mode Analysis of Liquid HF

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We present an instantaneous normal mode analysis of liquid HF aimed at clarifying the origin of peculiar dynamical properties which are supposed to stem from the arrangement of molecules in a linear hydrogen-bonded network. The present study shows that this approach is a unique tool for the understanding of the spectral features revealed in the analysis of both single molecule and collective quantities. For the system under investigation, we demonstrate the relevance of hydrogen-bonding "stretching" and fast librational motion in the interpretation of these features.

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In recent years, the analysis of instantaneous normal modes (INM) of normal and supercooled liquids has given a sound improvement to the understanding of the microscopic processes underlying the dynamical properties of these systems. Applications of the method are to be found in the calculation of macroscopic quantities through the knowledge of the density of states (e.g., the diffusion coefficient [1]) and in the interpretation of atomic motion through the inspection of the eigenvectors [2–4]. This last method appears to be a unique tool for the interpretation of dynamical features (single molecule or collective) of a disordered system in terms of correlated motions of its constituents. In particular, it is interesting to explore how the presence of locally ordered units is reflected in the time behavior of, for example, the velocity autocorrelation function (VACF). Attempts in this direction have to be found in the analyses of the following: (i) the correlation function of the projection of the center of mass (CoM) velocity of water molecules along the directions of the normal coordinates of a cluster of three molecules [5]; and (ii) the projection of INM eigenvectors onto the totally symmetric displacement coordinates of  $\text{ZnCl}_4^{2-}$  tetrahedral units [2]. Moreover, the INM approach has been exploited to describe the dynamical features of molecular liquids (e.g., diatomic Lennard-Jones [6],  $\text{CS}_2$  [7]) including hydrogen bonded systems such as water [3,8]. On the other hand, recent molecular dynamics simulations of HF have revealed peculiar dynamical features, e.g., a peak at  $\approx 50 \text{ ps}^{-1}$  in the spectra of both collective and single molecule correlation functions [9,10]. In the collective longitudinal and transverse current spectra this mode appears to have an optical-like character, since its frequency is found to be independent of the wave vector. For the interpretation of the CoM VACF spectrum, this peak has been related to the relative motion of two nearest neighbor molecules [10]. Since nearest neighbors are also hydrogen-bonded it is tempting to assign this dynamical feature to hydrogen-bonding "stretching." As a matter of fact, HF molecules have been demonstrated to form irregular zigzag chains of different size, being this peculiar clustering favored by the geometry of the molecule and the strong electrostatic inter-

action [11]. A dynamical characterization of these ordered units has not yet been given, so that any assignment of the spectral features to a particular dynamical process remains speculative.

In the present Letter we report the results of an INM analysis of liquid HF aimed to give an answer to the above problems. It will be shown to which extent the presence of irregular chains is reflected in the INM spectra and how the appearance of optical-like modes can be understood from the analysis of the short time dynamics naturally expressed by the INM eigenvectors.

The use of the INM analysis starts from the solution of the eigenvalue problem,

$$\omega^2 \mathbf{T} \mathbf{e} = \mathbf{K} \mathbf{e}, \quad (1)$$

where  $\mathbf{T}$  is the mass matrix of the system and  $\mathbf{K}$  is the matrix of the second derivatives of the potential energy. Here  $\mathbf{e}$  represents a multidimensional vector which specifies the instantaneous configuration of the system, i.e., in general, the three CoM coordinates and Euler angles of the assumed rigid molecule. An average over many independent configurations has to be performed in order to obtain the distribution of eigenfrequencies and any dynamical quantity derived from the knowledge of the eigenvector  $\mathbf{e}$ . In order to avoid spurious effects originating in the fact that the mass matrix  $\mathbf{T}$ , which depends on the sine of the polar angle, is not guaranteed to be strictly positive definite at each time, we have used the orientational coordinates described in Ref. [12] to evaluate the derivatives of the potential energy.

We have calculated the INM for liquid HF (at  $T = 203 \text{ K}$  and  $\rho = 1.178 \text{ g/cm}^3$ ), using 60 configurations separated by 2 ps with  $N = 108$  molecules. The potential model, reported in Ref. [13], accounts for the interaction of three fractional charges plus a Lennard-Jones contribution, and it has been shown to satisfactorily reproduce the thermodynamics and structure of the liquid. Because of the complexity of the interaction potential we have evaluated the matrix of the second derivatives numerically by displacing each generalized coordinate with

an increment  $h = 10^{-5} \text{ \AA}$  since it gives a good stability of the matrix elements and no unusually high eigenvalues. We also checked the accuracy of the results by the presence of three eigenmodes with zero frequency. Our value of the increment is in accordance with the one used, for example, in Ref. [14]. The generalized eigenvalue problem was resolved using standard methods [15].

The INM spectrum is presented in Fig. 1. A comparison with the results for water at room temperature (reported in Ref. [8]) points out some important features. The contribution of imaginary modes (conventionally reported on the negative axis) is substantially larger in HF than in  $\text{H}_2\text{O}$  (16% against 6%), a result consistent with the relatively higher diffusion coefficient found in HF [10]. Moreover, there is a much more definite separation between translational and rotational contributions defined by

$$\rho_T(\omega) = \left\langle \sum_i \sum_{\mu=1,2,3} (\mathbf{e}_{i\mu}^\alpha)^2 \delta(\omega - \omega_\alpha) \right\rangle, \quad (2)$$

$$\rho_R(\omega) = \left\langle \sum_i \sum_{\mu=4,5} (\mathbf{e}_{i\mu}^\alpha)^2 \delta(\omega - \omega_\alpha) \right\rangle, \quad (3)$$

where  $\mathbf{e}_{i\mu}^\alpha$  is the component of the eigenvector corresponding to the frequency  $\alpha$ , referred to the  $i$ th molecule and to coordinate component  $\mu$  ( $\mu = 1, 2, 3$  CoM,  $\mu = 4, 5$  rotational coordinates).

The rotational spectrum extends from 50 to 250  $\text{ps}^{-1}$ , whereas in water it goes from 0 to 180  $\text{ps}^{-1}$ . The translational spectrum of HF shows a clear second maximum at  $\approx 50 \text{ ps}^{-1}$  absent in the spectrum of water where one can notice only an asymmetry of the low frequency maximum with a larger content at higher frequency. We believe (and demonstrate later) that this secondary maximum is related to the stretching of the hydrogen bond between two HF

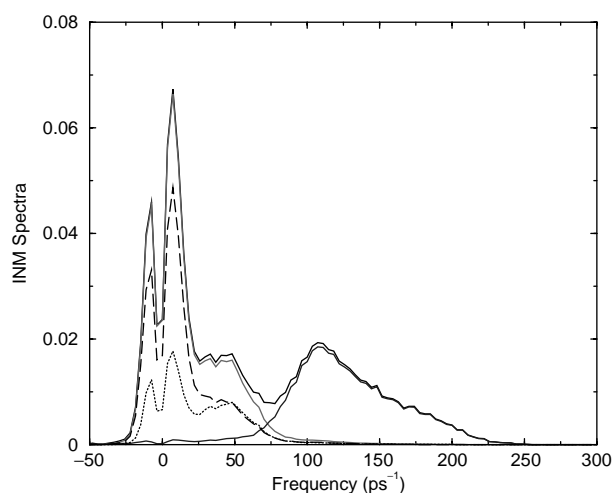


FIG. 1. Spectrum of the INM, with imaginary frequencies reported in the negative part, as usual. The thick line is the total spectrum, and has been divided into translational and rotational components, the latter of which appears only at high frequency. The dotted and dashed lines correspond to the contribution parallel and perpendicular to the molecular axis, respectively.

molecules. A comparison with the spectrum of the CoM VACF [10] points out that the peak at  $\approx 50 \text{ ps}^{-1}$  is much less pronounced and separated in the translational component of the INM.

The strong anisotropy of the single molecule dynamics is shown by performing a projection of the translational component of the eigenvector along the directions parallel and perpendicular to the molecular axis:

$$\rho_{\parallel}(\omega) = \left\langle \sum_i \sum_{\mu=1,2,3} (\mathbf{e}_{i\mu}^\alpha \mathbf{u}_{i\mu})^2 \delta(\omega - \omega_\alpha) \right\rangle, \quad (4)$$

where  $\mathbf{u}_i$  is a unit vector along the symmetry axis of molecule  $i$ , and we have also defined  $\rho_{\perp}(\omega) = \rho_T(\omega) - \rho_{\parallel}(\omega)$ . If the molecular motion were isotropic, the ratio between the perpendicular and parallel contributions would be equal to 2. Figure 2 shows that below 20  $\text{ps}^{-1}$  this ratio becomes larger than 2 going over 4 for modes at negative frequencies: a result which points out that molecules can diffuse more freely in the direction perpendicular to their axis rather than in the parallel one. Beyond 50  $\text{ps}^{-1}$  the ratio becomes equal or less than 1, thus revealing that the motion of the molecules in this frequency range occurs, on a large extent, in the direction of the molecular axis. Such an observation will be relevant in discussing the arrangement of molecules along irregular chains as revealed by the subsequent analysis of the INM eigenvectors. As a final remark, we wish to point out that the clear separation between translational and rotational components can be considered as a print of hydrogen bonded systems. In fact it is present in water and HF but not in a linear Lennard-Jones diatomic which has been investigated in [6].

To analyze in more detail the structure of the INM, we need to determine which molecules participate in each given mode. We assume the following criterion: the molecule  $i$  said to belong to mode  $\alpha$  if the condition  $\sum_{\mu} (\mathbf{e}_{i\mu}^\alpha)^2 > \frac{1}{N}$  is fulfilled. The distribution of the number of molecules per mode is reported in Fig. 3 (solid line) as a

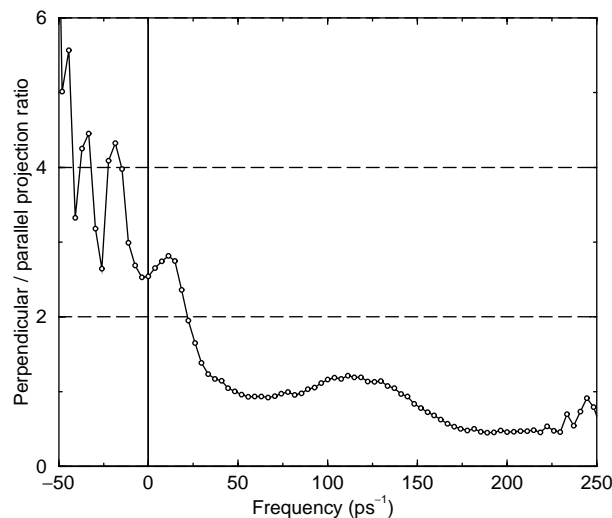


FIG. 2. The ratio between  $\rho_{\perp}(\omega)$  and  $\rho_{\parallel}(\omega)$  [see Eq. (4)]. It should be 2 for an isotropic system.

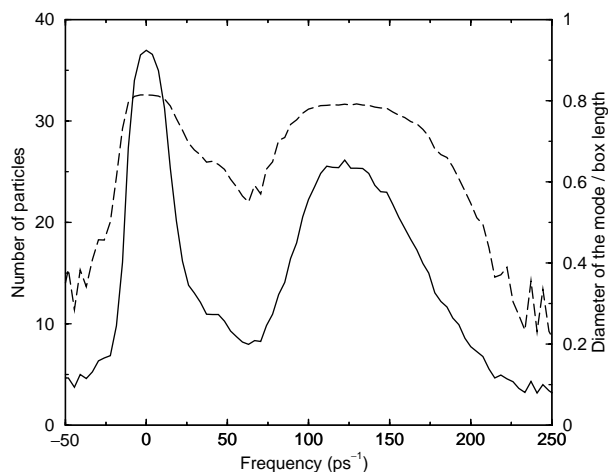


FIG. 3. Solid line (left scale): Frequency distribution of the particles participating in the modes. Dashed line (right scale): The distribution of the mode radii, normalized with the simulation box length (14.504 Å).

function of frequency. Knowing the particles participating in a given mode, we can determine the spatial localization of the mode.

If  $\mathbf{r}_i$  is the CoM position of particle  $i$  and  $S_\alpha$  is the set of particles involved in the mode, we can define a “radius” for the mode as the maximum distance between two particles, i.e.,  $R_\alpha = \max_{i,j \in S_\alpha} |\mathbf{r}_i - \mathbf{r}_j|$ , the distribution of which is reported in Fig. 3 (dashed line). A comparison of the behavior of the two quantities indicates a clear correspondence between participation ratio and extension of the modes. A lower number of participating molecules is accompanied by a smaller radius of the mode. Surprisingly enough, however, in the range of  $\approx 50 \text{ ps}^{-1}$  the modes have an extension of about half of the box length even if the number of molecules participating is smaller than ten.

A better understanding of this localization problem can be obtained by performing a projection of a mode onto the hydrogen bonded chains present in the system, where hydrogen bonding is defined by the same energetic criterion adopted in Ref. [13]. If  $C_c$  denotes the set of molecules belonging to the chain  $c$ , we define the projection of the mode  $\alpha$  on the chain as

$$P_{C_c}^\alpha = \sum_{i \in C_c, \mu} (\mathbf{e}_{i\mu}^\alpha)^2, \quad (5)$$

which is one if the mode  $\alpha$  is localized on the chain  $c$ , and is zero if the mode  $\alpha$  involves molecules not belonging to the chain. Clearly, if we consider the maximum of this projection taken on the set of all the chains, we can see whether the modes are localized on some chain or not.

The result presented in Fig. 4 (dashed line) indicates that, only in some frequency range, the modes show a high degree of localization on a single chain, in particular, in the same range where a minimum participation ratio occurs and the radius of the mode is lower (see Fig. 3).

The idea that modes at particular frequencies are strongly correlated to the presence of chains is confirmed

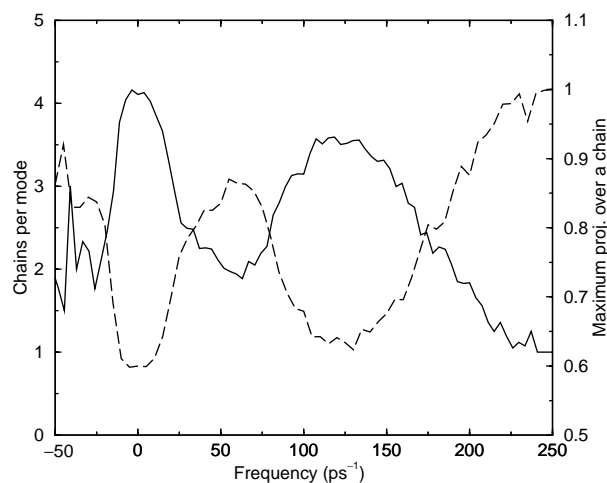


FIG. 4. Solid line (left scale): Frequency distribution for the number of chains involved in the modes. Dashed line (right scale): Frequency dependence of the mean value of the maximum projection of the eigenmodes onto a chain.

by looking at the distribution of the number of chains involved in a mode as reported in Fig. 4 (solid line). In the range  $\approx 50 \text{ ps}^{-1}$  (and in the region of imaginary frequencies) we find that the modes are spread over two distinct chains; at the highest frequencies only one chain per mode is involved. Since in this range only four molecules are participating to the mode (see Fig. 3), we can conclude that these modes are confined on the ring chains (tetramers) which are found to be particularly stable [13].

Having said that, it is also evident that most of the modes are far from being localized over a single chain, e.g., all the modes whose maximum projection is less than 0.80. This result is in accordance with other INM studies of network forming systems [2], where it is shown that the modes do not typically reproduce the behavior that could be expected on the basis of the group properties of the network, but generally have some sort of mixed character.

In order to characterize the spatial correlation of the molecular displacements through the INM eigenvectors, we have examined the following quantity:

$$\psi(R, \omega) = \left\langle \frac{1}{3N} \sum_{\alpha} \frac{1}{n(R)} \sum_{|\mathbf{r}_i - \mathbf{r}_j| \in R} \times \sum_{\mu=1,2,3} \mathbf{e}_{i\mu}^\alpha \mathbf{e}_{j\mu}^\alpha \delta(\omega - \omega_\alpha) \right\rangle, \quad (6)$$

where  $R$  denotes a spatial range (e.g., first or second shell of nearest neighbors, defined through the minima of the CoM pair correlation), and  $n(R)$  is the number of pairs present in that range for a given configuration. This quantity is a sort of mean value of the scalar product of the displacement of the particles being nearest or next-to-nearest neighbors in a given normal mode and at least at short time characterizes in an exact way the motion of the molecules participating to the particular mode. It is, of course, positive if the particles move in phase and

negative for out-of-phase displacements. The results are shown in Fig. 5.

We notice that the nearest neighbors have opposite phases in a broad frequency range around  $50 \text{ ps}^{-1}$ , a behavior in accordance with the presence of the stretching mode similar to the one observed in the solid [16] and consistent with the fact that, in this range of frequency, the molecules move preferentially along the direction of the molecular axis. We notice that the next-to-nearest neighbors are not very much correlated in this range, a signature of the fact that those modes are somehow localized over a chain (see Fig. 4) and do not involve many molecules, in agreement with the value of the participation ratio (see Fig. 3). The present result unambiguously confirms the optical-like character of the mode at  $50 \text{ ps}^{-1}$  present in the longitudinal and transverse current spectra reported in Ref. [9].

In a previous investigation of the collective properties of liquid HF [9], it has been shown that the longitudinal spectra have a peak,  $\omega_{\text{max}}$ , at low frequency, which changes linearly with the wave vector  $k$ . Its value is found to remain lower than  $10 \text{ ps}^{-1}$ . The corresponding phase velocity  $v_{\text{ph}} = \omega_{\text{max}}/k$  turns out to be somewhat higher than the ultrasonic (hydrodynamic) counterpart, but compatible with the presence of a positive anomalous dispersion as in the case of monatomic liquids (e.g., liquid metals). This feature is normally interpreted in terms of overdamped acoustic modes propagating in the system at wave vectors well beyond the hydrodynamic range. The results of the present INM analysis are consistent with such an interpretation, since they show that in the range below  $10 \text{ ps}^{-1}$  (i) the participation ratio is large (see Fig. 3) and (ii) the short time displacements of nearest and next-to-nearest neighbors are in phase as one would expect

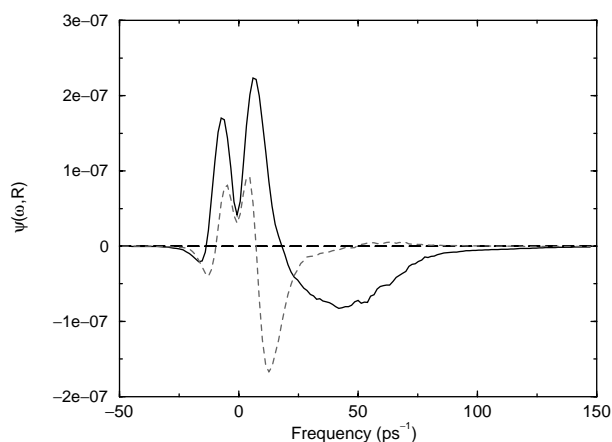


FIG. 5. The value of the spatial correlation between particles in various normal mode [see Eq. (6)]. The solid line shows correlation between the molecules being in the first shell, and the dashed line shows correlation between molecules in the second shell (multiplied by a factor of 5). The zero-frequency modes (corresponding to an overall translation of the system) have been dropped from the calculation.

from molecules participating to a collective (acousticlike) motion (see Fig. 5).

In conclusion, the INM analysis of HF has revealed how the dynamical features are affected by the presence of topological chains of hydrogen-bonded molecules. In certain ranges of frequencies there is a strict correspondence between INM modes and chains, where these modes are found to be localized. This result has allowed us to give a sound interpretation to a feature present both in the VACF and collective currents, namely, a peak at  $50 \text{ ps}^{-1}$  in the corresponding spectra. Such a characteristic can in fact be assigned to the stretching of hydrogen bonding of first neighboring molecules. This finding reveals the “optical” character of the collective mode present in the currents. Low frequency modes are found to be spread over the whole system involving several different chains, however they are confined to frequencies not much higher than  $10 \text{ ps}^{-1}$  in agreement with previous findings derived from the analysis of the longitudinal and transverse currents. The very high frequency (rotational) modes ( $\approx 200 \text{ ps}^{-1}$ ) are demonstrated to be confined over the highly stable tetramer chains.

Finally, we wish to stress the fact that our present study has the potential to pave the way for an unambiguous interpretation of the dynamical feature of other hydrogen-bonded systems (e.g., water) which are still a matter of a large debate.

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