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Author's Review

Infrared Band Shapes of van der Waals and Hydrogen Bonded Liquids. Comparison of Band Shaping Mechanisms

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Mechanisms shaping infrared absorption bands of Van der Waals and hydrogen bonded liquids are presented. Spectral activity of various rotational, vibrational and collision-induced relaxation mechanisms is compared. The structure of the hydrogen stretching band of molecules with hydrogen bonds is discussed in this general frame.

INTRODUCTION

Spectral manifestations of hydrogen bonding on hydrogen stretching infrared bands have been extensively investigated the last fifty years and have been described in several excellent text-books¹. The interpretation of these effects turned out to be unexpectedly difficult. This difficulty is due, not only to the intrinsic complexity of the problem, but also to the absence, except in recent years, of the basic theory of infrared band shapes of condensed phases. The situation has improved considerably in the last decade and numerous systems have been investigated containing, or not, hydrogen bonds. Basic mechanisms shaping infrared bands of liquids have been detected and some of them been examined in detail. Compare with Ref. 2—7.

The purpose of the present paper is to compare various band shaping mechanisms operative in Van der Waals and hydrogen-bonded liquids and to discuss why these two groups of liquids behave so differently. The ultimate reason for this difference is the fact that the H-bond interaction energy depends extraordinarily strongly on the AH and AH...B distances. No other shaping mechanism exists having a comparable spectral activity.

BASIC THEORY

The theory of infrared band shapes rests on a formula relating the infrared absorption coefficient $\alpha(\omega)$ to the dipole moment correlation function. If M denotes the macroscopic dipole moment of the liquid sample S , V its volume, n the refractive index and ω the frequency at which absorption is measured one can write⁸:

$$\alpha(\omega) = \frac{2\pi}{3c\hbar nV} \omega \left(1 - e^{-\frac{\hbar\omega}{KT}}\right) \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \vec{M}(0) \vec{M}(t) \rangle \quad (1)$$

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* Festschrift of Professor Dušan Hadži.

This formula represents one of the numerous formulations of the fluctuation-dissipation theorem; microscopic fluctuations of the dipole moment \vec{M} generate macroscopic dissipation of the infrared radiation. The problem of analyzing bands shapes thus reduces to that of calculating the correlation function, $G(t) = \langle \vec{M}(0) \vec{M}(t) \rangle$.

The theories built to calculate $G(t)$ are all semi-classical. Vibrational degrees of freedom are generally treated in the frame of quantum mechanics whereas rotational and translational degrees of freedom are always considered to be classical, since purely quantum mechanical approach is not practicable at the present time. In turn, the classical N-body problem associated with translations and rotations may conveniently be examined either by a computer or by a stochastic simulation and both these techniques have been employed with success. It should also be emphasized that the semiclassical techniques just mentioned have been well explored and can safely be applied except at low temperatures.

ROTATIONAL BAND SHAPING MECHANISMS

Molecular rotations may conveniently be described by their angular velocity vector $\vec{\Omega}(t)$ whose correlation time, τ_Ω , may be compared with $\tau = \sqrt{\frac{I}{KT}}$ where I is a representative value of molecular moments of inertia. If $\tau_\Omega \gg \tau$, the angular velocity $\vec{\Omega}(t)$ maintains its coherence over a period long as compared with the time of a single revolution and the rotation appears as a free rotation. If $\tau_\Omega \ll \tau$, the coherence of the angular velocity is lost much before a single revolution is accomplished and the rotation appears as a rotational diffusion. Finally, if $\tau_\Omega \sim \tau$, the rotation is intermediate between the free rotation and the rotational diffusion, a motion generally termed as extended or generalized diffusion. The theory has been elaborated for all types of molecular rotors and for all ratios τ_Ω/τ . Compare with Ref. 3—5.

This theory shows that the spectral density depends on the type of molecular rotation as well as on the direction of the transition moment in the molecule-fixed frame. Some representative band shapes of an asymmetric rotor taken from Ref. 9 are illustrated in Figures (1a—d); the strength of molecular interaction is increasing when going from Figures (1a) to Figures (1d). In the free rotation limit the band exhibits a more or less complicated central peak as well as two wings; the overall width of the spectral pattern is of the order of $\sqrt{\frac{I}{KT}}$. In the presence of a weak intermolecular perturbation, the fine structure of the central peak due to slow nutation- and precession-type motions collapses and a typical three-component P, Q, R-type structure appears. The latter collapses, in turn, when the perturbation is stronger. In the last stage one finds either a Lorentzian or a superposition of Lorentzians; the half-width of the band is of the order of D , a representative value of the rotational diffusion constant. Now inertial effects have disappeared and the spectral density is that of a Markovian-Gaussian process.

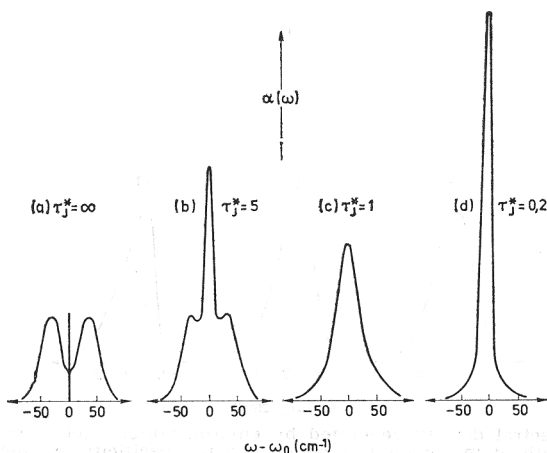


Figure 1. Infrared spectral density of an asymmetric rotor. The direction of the transition moment is along the axis of smallest moment of inertia. $\tau_J^* = \sqrt{\frac{KT}{I_Y}} \tau_J$ where τ_J is the mean collision time of the J -diffusion model. For details, see Ref. 9.

VIBRATIONAL BAND SHAPING MECHANISMS

a) Generalities. Vibrational relaxation is due to the coupling between internal vibrational and external rotational-translational degrees of freedom of a liquid sample. This process is generated by a large variety of inter- or intramolecular forces, including the dipole-dipole, dipole-induced dipole, dispersion, short range repulsion forces and hydrogen bonding. The relaxation due to centrifugal or Coriolis forces is generally, although arbitrarily, separated from the present context and is studied in the theory of rotational relaxation. Vibrational relaxation originates either in de-excitation or in dephasing of molecular vibrations; these processes are called T_1 and T_2 processes, respectively, in agreement with the well known terminology of nuclear magnetic resonance. The theory of vibrational relaxation processes is recent and still incomplete^{6,7}. Some basic band shaping processes are described in what follows.

b) Environmental Fluctuations of the Vibrational Frequency. The simplest mechanism generating vibrational relaxation is connected with fluctuations of the vibrational frequency $\omega_{10}(t)$ of a molecule. In turn, these fluctuations are generated by fluctuations of the molecular environment in the liquid phase. This process represents a pure dephasing and the correlation function $G(t)$ reaches vanishingly small values for times t such that the dispersion in the phase $\varphi(t) = \int_0^t dt' \omega_{10}(t')$ is of the order of unity. If the variations of $\omega_{10}(t)$ are slow enough, i. e. if the correlation time τ of $\omega_{10}(t)$ is much longer than the time scale $1/\Delta\omega_{1/2}$ of the experiment, the band shaping mechanism is termed inhomogeneous and the observed profile can then be viewed as reflecting the static distribution of transition frequencies; see the Appendix. Some representative band shapes generated by this process are illustrated on Figures (2a—c) for the case of a diatomic molecule in solution; the solvent-

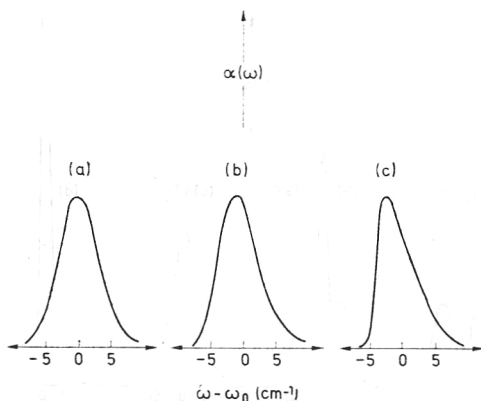


Figure 2. Infrared spectral density generated by environmental fluctuations of the vibrational frequency. The strength of molecular interaction and its specificity are increasing when going from Figure 2a to Figure 2c. For details, see Ref. 10.

-solute interaction becomes progressively more specific when going from Figures (2a) to (2c). $\Delta\omega_{1/2}$ has the values, following the speed of molecular fluctuations, between $\sqrt{\langle[\omega_{10}(0) - \langle\omega_{10}(0)\rangle]^2\rangle}$ and $\langle[\omega_{10}(0) - \langle\omega_{10}(0)\rangle]^2\rangle \tau$ where

$$\omega_{10}(t) = \frac{1}{2\mu\omega_0} \left[-\frac{f}{K} \left(\frac{\partial V(nt)}{\partial n} \right)_{n=0} + \left(\frac{\partial^2 V(nt)}{\partial n^2} \right)_{n=0} \right] \quad (2)$$

In this formula, valid for a diatomic vibrator, μ represents its reduced mass, ω_0 the non perturbed vibrational frequency, k the harmonic and f the cubic force constant. Moreover, $\left(\frac{\partial V}{\partial r}\right)$ and $\left(\frac{\partial^2 V}{\partial r^2}\right)$ denote the derivatives of the randomly fluctuating molecular interaction energy $V(r, t)$ with respect to the vibrational coordinate r^{10} . One concludes that, if the environmental fluctuations of the vibrational frequency constitute the dominating band shaping mechanism, the band width depends, essentially, on the statistical dispersion of the transition frequency $\omega_{10}(0)$; larger are the fluctuations of this quantity broader is the band.

c) *Geometrical Fluctuations of the Vibrational Frequency.* This mechanism represents a variant of that described in the previous Section. It is operative whenever the molecular interaction is strong enough to generate complexes such that their life time is long compared with the time scale $1/\Delta\omega_{1/2}$ of an infrared experiment; this is particularly the case for the hydrogen bonded liquids. Vibrational relaxation is then due to the fluctuations of the vibrational frequency $\omega_{10}(t)$ induced, in turn, by the fluctuations of the geometry of the complex; this is a pure dephasing. Since the correlation time, τ , of $\omega_{10}(t)$ is generally large compared with $1/\Delta\omega_{1/2}$, inhomogeneous broadening is produced. A typical band shape produced by this mechanism is illustrated on Figures (3); it corresponds to the $1 \nu_{AH}$ band of a molecule containing a weak hydrogen bond. Its profile is a asymmetrical distorted Gaussian whose half-width is of the order of $\sqrt{\langle[\omega_{10}(0) - \langle\omega_{10}(0)\rangle]^2\rangle}$, where $\omega_{10}(t)$ still is given by Eqn. (2) of Section 4b. However, $V(t) = V(r, R_1(t), R_2(t) \dots R_6(t))$ is now the energy of

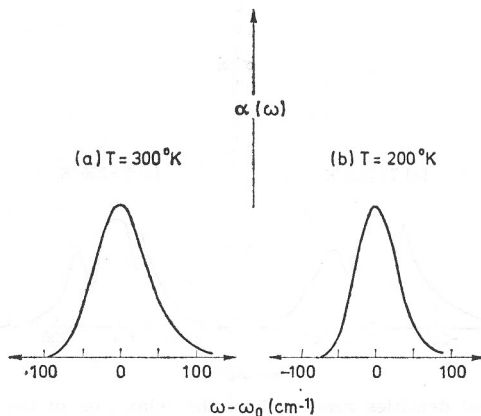


Figure 3. Infrared spectral density generated by the geometry fluctuations of an H-bonded complex; two different temperatures are considered. For details, see Ref. 11.

anharmonic interaction between the internal hydrogen stretching mode r and the six bath driven external modes $R_1(t), R_2(t) \dots R_6(t)$. This is due to the fact that the interaction energy is large enough to transform, in time scales of interest, large amplitude rotational-translational motions to small amplitude intermolecular vibrational motions. Here again, the band width depends on the statistical dispersion of the vibrational frequency $\omega_{10}(0)$; the $1 \nu AH$ band is exceptionally broad because the statistical fluctuations of this quantity are exceptionally large. A detailed calculation shows that the half-width of this band is of the order of $\sqrt{\frac{\omega'^2 K_B T}{k}}$ where ω' is the derivative of the frequency of the νAH mode with respect to the $AH \dots B$ distance, k the harmonic force constant of the bridge vibration, T the absolute temperature and K_B the Boltzmann constant¹¹.

d) *Quasi-resonant Intramolecular Vibrational Coupling.* This mechanism generates processes in which two or several modes of a given molecule, coupled by an appropriate mechanism, undergo a simultaneous relaxation. They can not be considered, in general, as T_1 or T_2 processes but have mixed characteristic. The most familiar coupling mechanism occurring in systems with hydrogen bonds is the Fermi resonance between the quasi-degenerate mono-excited hydrogen stretching and some doubly-excited harmonic levels. The $1 \nu AH$ level can also be coupled to other closely lying singly excited harmonic levels through the appropriate component of the intermolecular potential. The spectral density generated by these intricate processes which always are coupled to the fluctuations of the vibrational frequency is exceptionally complex; compare with Figures (4a, b). The band profile exhibits either a broad and diffuse structure or narrow transmission windows. The theory shows that broad and strongly interacting combination bands produce flat and broad structures whereas narrow and weakly interacting combination bands generate fine transmission windows. These processes are thus characterized by a phenomenology of a considerable breadth; not all of them have as yet been investigated¹².

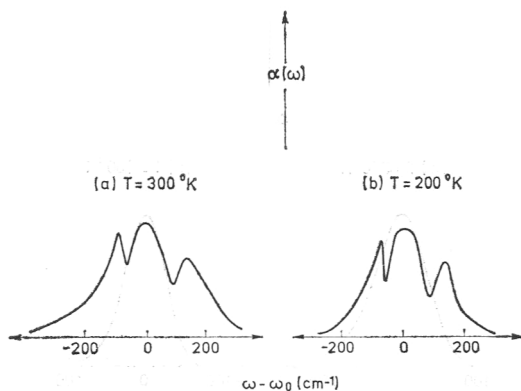


Figure 4. Infrared spectral densities generated by the relaxation of the modes ν_{AH} , δ_{AH} , γ_{AH} coupled through the Fermi resonance; two different temperatures are considered. For details, see Ref. 11.

Three other band shaping mechanisms are the resonant and non-resonant intermolecular and the non-resonant intramolecular coupling. The first has recently been investigated by several authors in the case of pure Van der Waals liquids. According to the theory, its spectral activity is very small in infrared although it is moderately large in isotopic Raman¹³. The remaining two mechanisms have not yet been analysed in detail and their spectral manifestations are not well known.

COLLISION-INDUCED BAND SHAPING MECHANISMS

Collision-induced absorption arises from transient dipoles produced by distortion of the electronic distribution of molecules in binary, ternary and higher order interactions. The long lived complexes, e. g. in hydrogen-bonded liquids, are generally not considered in this context; they are described as independent, stable entities. The collision-induced dipole moment is generated by long range multipolar and short-range electron overlap forces. This pair dipole is modulated by the vibration and rotation of the colliding molecules and, because of its strong dependence on the intermolecular separation, by their relative translational motions. There results a variety of collision-induced spectra which can be observed most conveniently in the case of normally forbidden bands where all competing processes are absent. The profiles expected in Van der Waals liquids are illustrated, schematically, on Figures (5a, b); one

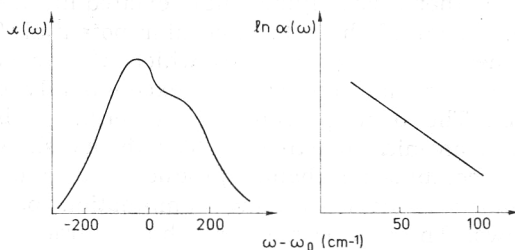


Figure 5. Infrared collision-induced spectral density (schematic). Molecular rotations are relatively free in the case of Figure (5a) and are strongly hindered in the case of Figure (5b).

notices, in particular, the straight line aspect of the spectral density on a logarithmic plot. No quantitative theory of these processes is as yet available for liquids; however, the situation may change rapidly in next few years¹⁴.

COMPARISON OF BAND SHAPES AND DISCUSSION

The first observation concerns the extraordinary richness of mechanisms shaping infrared bands of liquids. Their spectral activity depends on the physical and chemical properties of the systems under investigation. As a rule, rotational band shaping mechanisms dominate the spectral behavior if molecular interactions are weak and if molecular moments of inertia are small; the inertial effects are sometimes strongly pronounced. The importance of vibrational relaxation mechanisms increases with increasing strength of molecular interaction with hydrogen bonding representing the most extreme example of this type. Finally, the collision-induced band shaping processes are omnipresent but their role is not yet entirely understood. Thus results a large variety of possible band profiles. A hope was expressed in early days of this subject that it would be possible to describe infrared band shapes of liquids by the help of simple Lorentzians or Gaussians; this hope however was not confirmed by the subsequent work.

Why are the hydrogen stretching bands of molecules with hydrogen bonds so different from all other bands? In all cases where the profiles are generated by environmental, or geometrical fluctuations of transition frequency, the band width depends on the statistical dispersion of the transition frequency $\omega_{10}(0)$. This dispersion which is particularly large in hydrogen bonded liquids is due to a large anharmonic coupling between the νAH and $\nu AH \dots B$ motions. The ultimate reason for the existence of this effect is to be found in the electronic structure of a hydrogen bond. The electrostatic, charge-transfer, dispersion and short range repulsion forces which contribute to its energy balance in a delicate way and render it extremely sensitive to the AH and AH \dots B distances.

A final comment concerns the terminology employed in this paper. This terminology corresponds to that in use in the theory of infrared and Raman band shapes of liquids but differs, to a certain extent, from the one applied in the theory of hydrogen bonding. Its use is advisable in order to accelerate the unification of the theory which seems possible in the present situation.

REFERENCES

1. G. C. Pimentel and A. L. Mc Clellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960), Chap. 3 pp 67—141.
2. R. T. Bailey, *Mol. Spectrosc.* 2 (1974) 173.
3. J. E. Griffiths, *Vibrational Spectra and Structure* 6 (1977) 273.
4. W. A. Steele, *Adv. Chem. Phys.* 34 (1976) 1.
5. W. A. Steele, in *Intermolecular Spectroscopy and Dynamical Properties of Dense Systems*, J. Van Kranendonk Editor (North Holland, Amsterdam, 1980), pp 325—374.
6. D. W. Oxtoby, *Adv. Chem. Phys.* 40 (1978) 1.
7. S. Bratos, in *Vibrational Spectroscopy of Molecular Liquids and Solids*, S. Bratos and R. M. Pick Editors (Plenum, New York, 1980), pp. 43—60.
8. R. G. Gordon, *Adv. Mag. Res.* 3 (1968) 1.
9. J. Cl. Leicknam, Y. Guissani, *Mol. Phys.* 42 (1981) 1105.
10. S. Bratos, J. Rios, Y. Guissani, *J. Chem. Phys.* 52 (1970) 439.
11. S. Bratos, *J. Chem. Phys.* 63 (1975) 3499.

12. D. Hadzi, *Chimia* **26** (1972) 7.
 13. R. M. Lynden-Bell, *Mol. Phys.* **33** (1977) 907.
 14. G. Birnbaum, in *Vibrational Spectroscopy of Molecular Liquids and Solids*, S. Bratos and R. M. Pick Editors (Plenum, New York, 1980) pp 147–165.

APPENDIX

The dipole moment correlation function corresponding to a band generated by adiabatic fluctuations of transition frequency may be written¹⁰:

$$\overrightarrow{M}(0) \overrightarrow{M}(t) = \overrightarrow{M}(0)^2 \langle \exp [i \int_0^t dt' \omega_{10}(t')] \rangle \quad (\text{A.1})$$

If the fluctuations of $\omega_{10}(t)$ are slow and $\tau \gg 1/\Delta\omega_{1/2}$ it is legal to replace $\omega_{10}(t)$ by ω_{10} . Then, designating by $P(\omega_{10})$, the probability that the transition frequency is equal to ω_{10} , and by ω , the frequency at which the spectrum is observed, one can write:

$$\alpha(\omega) \sim \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' e^{-i\omega t'} \overrightarrow{M}(0) \overrightarrow{M}(t) \sim \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \langle e^{-i(\omega - \omega_{10})t} \rangle = \quad (\text{A.2})$$

$$= \int_{-\infty}^{\infty} \int dt' d\omega_{10} P(\omega_{10}) e^{-i(\omega - \omega_{10})t} = \int_{-\infty}^{\infty} d\omega_{10} P(\omega_{10}) \delta(\omega - \omega_{10}) = P(\omega)$$

The spectral density at ω is then proportional to the probability $P(\omega)$ that the transition frequency is equal to ω .

IZVLEČEK

Oblika nihajnih trakov van der Waalsovih tekočin in tekočin z vodikovimi vezmi. Primerjava mehanizmov, ki vplivajo na njihovo obliko

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Članek opisuje profile infrardečih spektrov Van der Waalsovih tekočin in tekočin z vodikovimi vezmi. Naslanja se na statistično teorijo spektralnih profilov in obravnava študij raznovrstnih relaksacijskih mehanizmov. Rotacijski relaksacijski mehanizmi posedujejo profile z močno izraženimi stranskimi trakovi, če je molekulska rotacija v tekočini dovolj prosta; če pa ni, ima profil obliko Lorentzove krivulje ali njih superpozicije. Nihajni relaksacijski mehanizmi predstavljajo bodisi energijsko, bodisi fazno relaksacijo. Fluktuacija lokalne strukture v tekočini in fluktuacija geometrije vodikovo vezanih kompleksov povzročata fazno relaksacijo. Ta je posebno hitra v prisotnosti vodikovih vezi. Prenos nihajne energije med sosednjima molekulama v tekočini prav tako pokaže pod pogoji resonance fazno relaksacijo. Zapleteni relaksacijski procesi v primeru tekočin s srednje močnimi ali močnimi vodikovimi vezmi vsebujejo istočasno elementarne fazne in energijske relaksacije. Končno, sprememba molekulskega dipolnega momenta in sprememba molekulskega tenzorja polarizirnosti pod vplivom molekulskih sil v tekočinah vodita do novih relaksacijskih procesov zelo specifičnih karakteristik. Velika širina trakov νOH v sistemih z vodikovimi vezmi je posledica zelo močne odvisnosti energije kompleksov od razdalje $\text{OH}\dots\text{O}$, fazna relaksacija je temu primerno hitra.