

# OPTICAL PROPERTIES AND MOLECULAR INTERACTIONS

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## ABSTRACT

This paper deals mainly with the modifications of molecular spectra when the density varies as a function of pressure and temperature. It represents a brief survey of some of the work conducted at Bellevue. The main topics covered are: (i) depolarized scattering of light by rare gases, due to anisotropic field fluctuations and atomic distortion; (ii) translational spectra in the far-infrared in dense rare gas media, and phonon bands, in solid rare gases; (iii) pressure induced spectra in the vibration-rotation region, in particular for hydrogen in solid argon, exhibiting localized and non-localized phonon bands; (iv) vibration-rotation spectrum of solid hydrogen up to 11 kbar pressure, revealing in particular the nature of the bands by the magnitude of their shifts; and (v) vacuum ultraviolet electronic spectra of some molecules trapped in rare gas matrices, or as pure solids; resonance line of pure solid Ne exhibiting very weak perturbation; deperturbation of NO valence transitions in a matrix, as observed under high resolution and with an improved model of the vacuum spark as a source.

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I would like to apologize in advance for not speaking exclusively on solid-state spectroscopy, thus breaking the 'selection rule' of this conference. I would like to present a brief survey of some of the researches developed at my laboratory, which show how the spectra of molecular solids (or dense media) change when the density is either decreased or increased by the combined effects of temperature and pressure, and which in particular indicate the relationship between the spectra in the solid state and those of the free molecule.

My paper corresponds essentially to the work of the following among my co-workers: Oksengorn and Thibeau, Dumartin and Triki: Vu and Marteau, Jean-Louis and others; H. Damany and Roncin, Boursey, Castex, etc.

The density of gases under pressures of several kilobars is about the same as the density of liquids and solids. Therefore the subject of my paper may be more relevant now, when pure molecular effects are beginning to be considered in crystals.

I shall begin with a description of the results involving the weakest excitation.

# 1. DEPOLARIZATION OF SCATTERED LIGHT BY COMPRESSED ARGON GAS

For a free spherical atom there is no depolarization. Molecular interactions produce anisotropic perturbations which should lead to depolarization<sup>1-3</sup>. Density fluctuations are responsible for the non-depolarized light-scattering intensity  $I$ . Anisotropic field fluctuations due to anisotropy of the density distribution constitute one source of depolarization of the scattered light (of intensity  $i$ ).

The results of Thibeau<sup>3</sup> showed three regions for the ratio  $i/I$  (Figure 1): the first corresponding to binary collisions, and then a slower increase, corresponding to a much slower increase of  $i$ , since  $I$  decreases strongly, the medium approaching liquid densities.

The decrease was interpreted as being due to an increased symmetry at high densities of the environment (Figure 2), i.e. by a cancellation effect. This shows that such studies can reveal the symmetry around a site in dense media<sup>4</sup>.

But the situation in reality is more complicated. Alder and co-workers<sup>5</sup> have calculated by a computer experiment the ratio  $(\beta/\alpha)^2$  (directly related to  $\Delta = i/I$ ) of the polarizability anisotropy  $\beta$  versus the mean anisotropy  $\alpha$ . The comparison with experimental data shows that the calculated values are much higher. This indicates that, as far as depolarization is concerned, local distortion of the electron clouds opposes the anisotropy created by density fluctuations.

In fact we have recently shown that the depolarization ratio decreases when the temperature is increased<sup>6</sup> (Figure 3). This seems to be a direct indication of a distortion effect since such an effect should be enhanced when the molecules collide with greater energies.

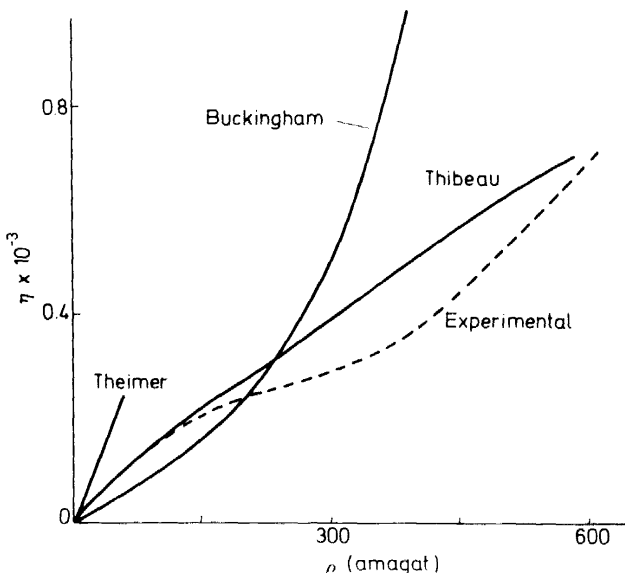
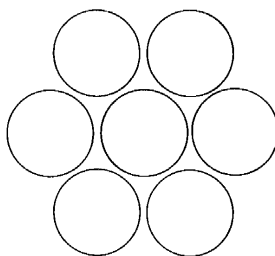


Figure 1. Comparison between experimental and theoretical values of the depolarization of light in argon, as a function of density (in amagat)

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If each atom has a homogeneous surrounding then the field fluctuations would be zero. At high density the environment becomes more symmetric and  $i \rightarrow 0$ . The dipoles of the neighbouring atoms then produce a zero field on the central atom



This can be seen in a regular distribution of the six perturbaters

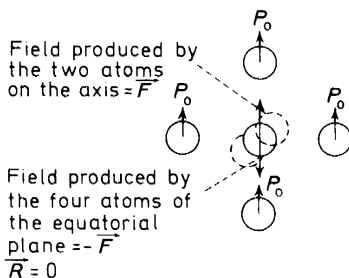


Figure 2. Elementary representation of the increased symmetry of the environment in a fluid at high densities

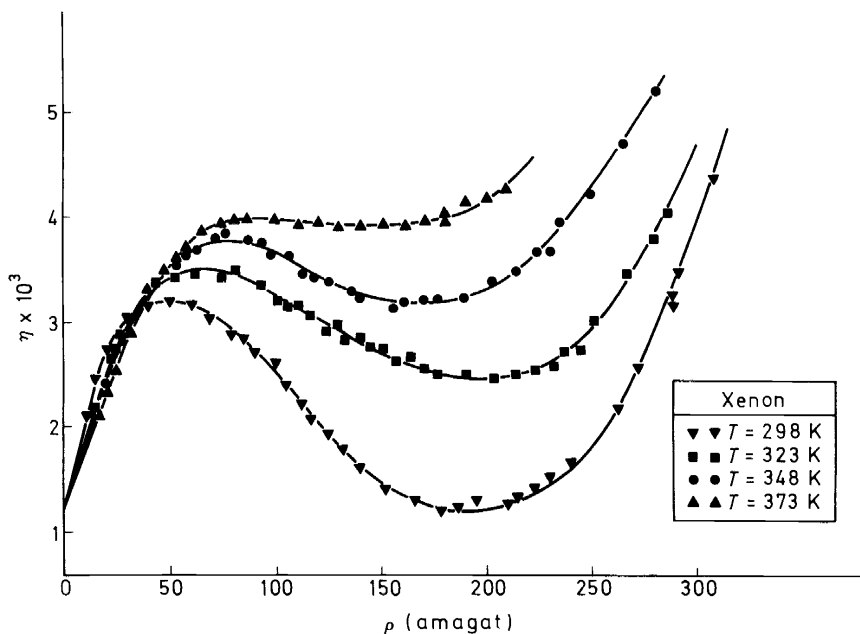


Figure 3. Temperature effect on the depolarization of light in a dense fluid (xenon)

## 2. TRANSLATIONAL FAR-I.R. SPECTRA OF RARE GASES

When two rare gas atoms fly past each other a dipole moment is induced, which is time dependent, because both the intermolecular distance and the orientation of the pair are changing. Therefore an i.r. spectrum is developed. At Bellevue we have worked at rather high pressures, and for the first time a quantitative view of the behaviour of a number of mixtures of rare gases was obtained<sup>7-9</sup>. Of course, in a pure gas, there is no effect, for reasons of symmetry of binary collisions. But one can expect an effect for multiple collisions, at high densities, provided that the symmetry of the environment is not too large.

The phenomenon is, strictly speaking, quantum mechanical: an approximate theory in that sense was developed. It is nevertheless sufficient to say that experimentally the behaviour of this phenomenon is kinetic. But a more refined point is more relevant for the present conference:

The probability of the transition of the low-energy side decreases steeply (Figure 4) whereas classically it should tend to a constant value<sup>10</sup>. This is an experimental confirmation of an important theoretical prediction of Van Kranendonk<sup>11</sup>, who expected this decrease to occur because of the correlation of the phenomena between collisions (which are in opposition to the 'molecular chaos' model). This effect seems to be the evidence for the correlations, which are a central point of the statistical mechanics of dense media, and were not observable in bulk properties such as transport properties.

This point brings us closer to the solid state. Let us go further. Indeed one can solidify by raising the pressure at constant temperature of one of the gases, and thus obtain a solid rare gas. Then the translation band becomes a

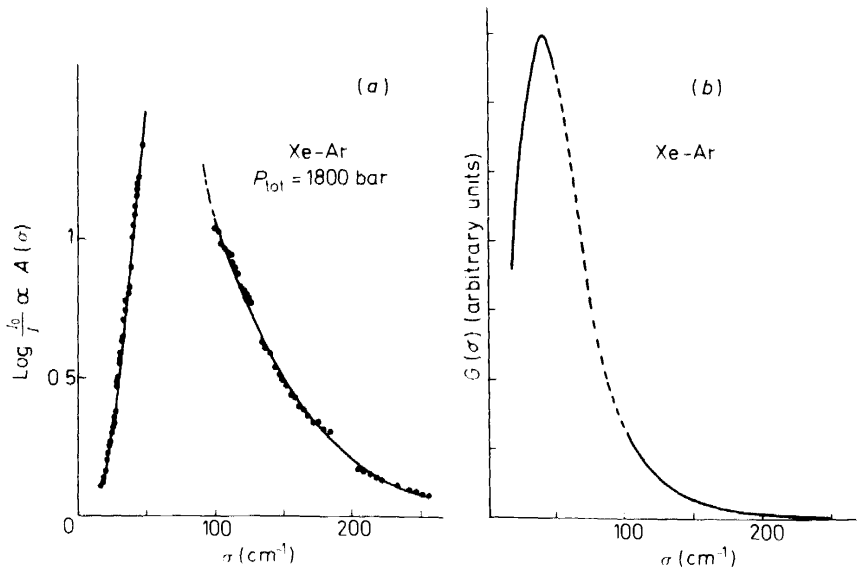


Figure 4. Translation band in Xe-Ar mixture: (a) opacity; (b) transition probability  $G(\sigma)$

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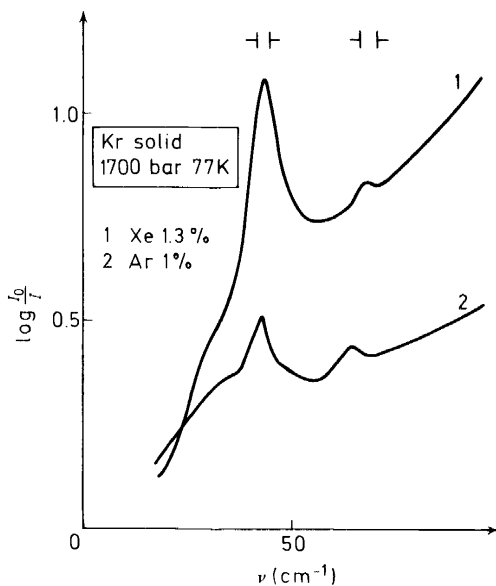


Figure 5. Phonon bands in the solid krypton matrix

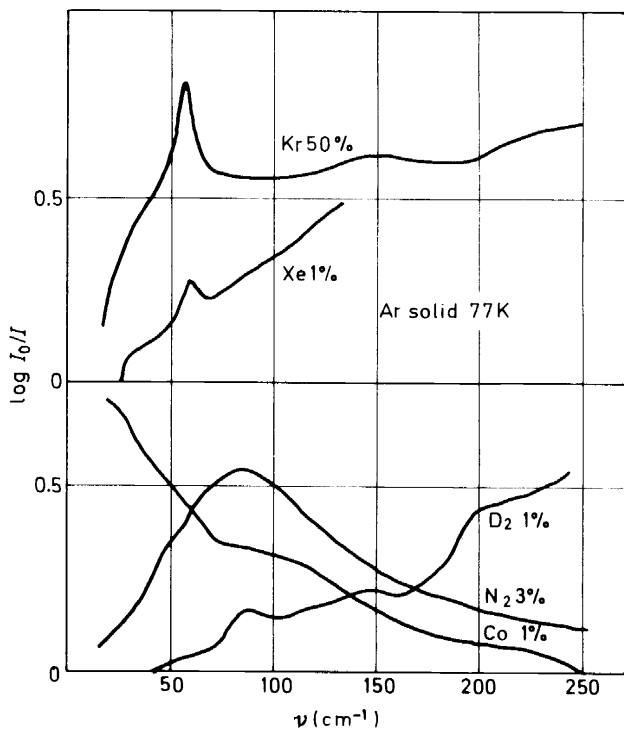
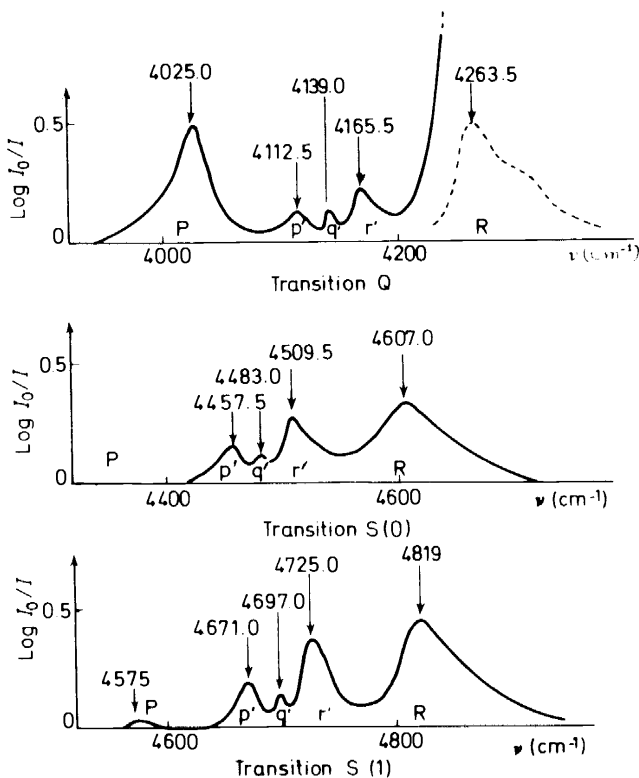


Figure 6. Phonon bands in the solid argon matrix

phonon band—either of the lattice (*Figure 5*, in Kr) or a localized (or pseudo-localized) phonon band: various molecules in solid argon are shown in *Figure 6*<sup>12</sup>.

With H<sub>2</sub> and D<sub>2</sub> in argon, long paths of solid argon up to 1 m were needed, since the solubility is not large. An interesting check was made—the frequency shift of the phonon band varies as the square root of the mass ratio—showing that the phonon band is purely localized in that case. This is shown in *Figure 7*<sup>13</sup>.



*Figure 7.* Absorption bands of H<sub>2</sub> in the solid argon matrix (p', r': non-localized phonon; P, R: localized phonon)

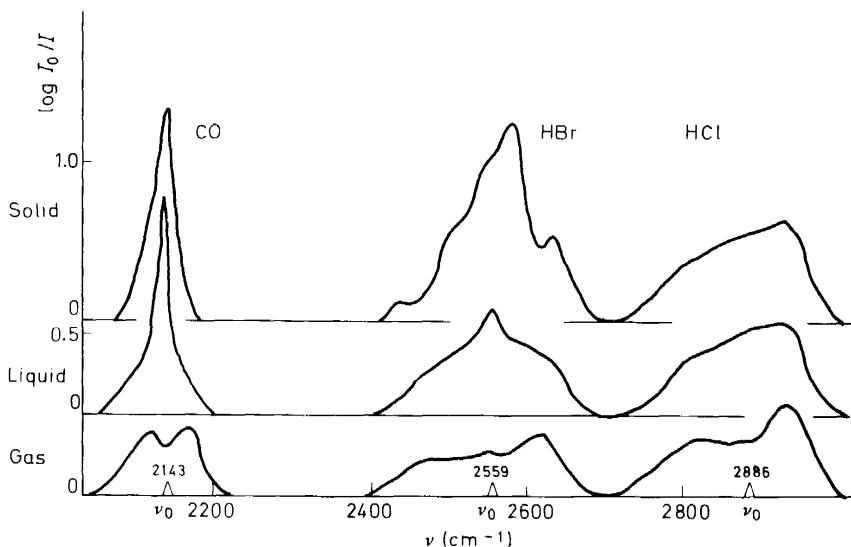
### 3. GAS PHASE STUDIES

This subject deals with pressure induced effects, sometimes superimposed with pre-existing permitted transitions such as in HCl<sup>14, 15</sup>.

Among the old results I shall only mention HCl mixed with foreign gases, as this had experimentally demonstrated the existence of van der Waals complexes and possibly of orbiting pairs. A collision induced band was observed near the forbidden Q branch. Now it is almost quantitatively interpreted as being due to a pair formation, followed by, in the pair, a rotational hindrance due to an anisotropic potential, such as the quadrupolar potential for N<sub>2</sub> for example, together with the effect of eccentricity of the

mass centre with respect to the charge centre. The evidence now is definitely supported by the fine structure which corresponds to the motion modes of the pair.

This complexing is to some extent connected with the general behaviour in dense media, since one observes a continuous modification of the spectra of HCl, HBr and CO in argon, as shown in *Figure 8*, from gaseous to liquid and solid states of argon.



*Figure 8.* Modification of vibration-rotation absorption bands of HCl, HBr and CO in argon, from gaseous to liquid and solid states

When the temperature is not low enough, diffusion takes place in the solid and clustering may be observed as a function of time, for example with HCl. The stages of formation of two or several molecules can be observed. This shows the progressive steps of building up a bulk molecular solid.

#### 4. SOLID-STATE STUDIES AS A FUNCTION OF PRESSURE

This is now the main subject of this group, but I shall restrict my description to only one example, solid H<sub>2</sub> as a function of pressure. Such results complement the famous data of Welsh and co-workers by giving information about the effect of the internuclear distances on the perturbations, since over the range covered the density is increased two-fold. For that purpose an original apparatus was designed in which the pressure can be varied continuously, up to 15 kbar and at low temperature, down to 2 K. As an example the v.r. spectrum of pure H<sub>2</sub> at 4.2 K, up to 11 kbar<sup>16</sup>, is shown in *Figure 9*. A considerable increase in the intensity of the bands is observed as the pressure is raised.

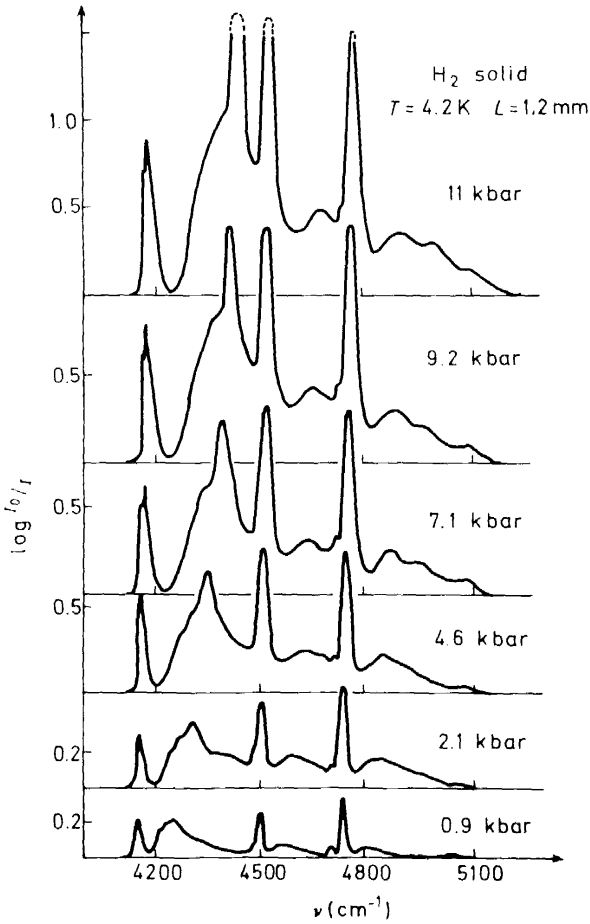


Figure 9. Pressure effect on the spectrum of solid  $H_2$ .

The spectrum at normal pressure is composed, as is well-known, of essentially simultaneous transitions combining  $H_2$  frequencies, plus phonon bands. The simple induced transitions are weak for reasons of symmetry, i.e. by virtue of the cancellation effect. A particularly strong increase in the  $Q_R$  band which is a phonon band due to overlap forces is observed. A similar behaviour for shifts is shown in Figure 10: the  $Q_{1q}$  so-called pure vibrational band, because of quadrupolar interactions, is shifted much less than the  $Q_R$  band. This is a characteristic example of a strong pressure associated with short-range interaction<sup>13</sup>.

Since we are in the Soviet Union I must mention here the general interest of studies on hydrogen at high pressure, i.e. the problem of metallic hydrogen, which is connected with the construction of the largest laboratory press ever built at the High Pressure Institute of the Akademia Nauk, supervised by Academician Vereshchagin. The general interest of such studies is connected with the problem of metallic hydrogen, which should appear near 3 Mb



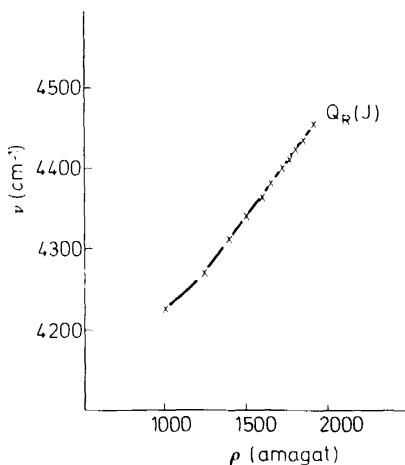
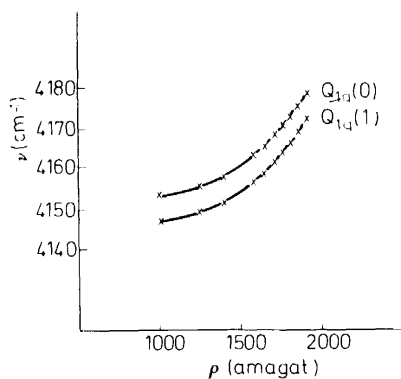


Figure 10. Comparison between shifts of the phonon band ( $Q_R$ ) and the vibrational band ( $Q_{1q}$ ) in solid  $H_2$  as a function of density

pressure—and the stability of which on returning to normal pressure will depend upon the energy of the phonon vibrations, and whose transition temperature  $T_c$  is related to a characteristic temperature which is approximately the  $Q_{Debye}$ . All data regarding the behaviour of phonon spectra, even in molecular hydrogen, can be helpful for the theory, since  $H_2$  is a quantum solid unstable below 1 kbar in the harmonic model.

Interpretation of the shifts is in progress. Unfortunately, as the results correspond only to normal  $H_2$  and not to its pure species the orientational part of the potential could not be introduced. However, two results should be cited :

(i) The intramolecular potential has been developed in series as a function of internuclear distance, plus the intermolecular potential versus the same parameter (according to Van Kranendonk). Experimental shift of the  $Q_J$  band is given to within 10 or 20 per cent.

(ii) For phonon bands, the vibration becomes more harmonic as the

pressure increases: accordingly the harmonic-model calculations seem justified: such a model gives the experimental shifts of the phonon band to within an accuracy of 10 per cent.

## 5. ELECTRONIC SPECTRA—SOLID STATE

These studies are made in the v.u.v. range and deal with a matrix condensed at low temperatures. For reaching shorter wavelengths the deposit is made on a fluorescent screen, and an original recording spectrophotometer was developed<sup>17</sup>, with a double beam and which operates with a Bellevue-type vacuum spark as source. Recently this source, used both in photoelectric and photographic spectroscopy, was considerably improved<sup>18</sup>. May I remind you that it is a three-electrode vacuum spark triggered by a sliding spark. By reducing the time constant and increasing the capacity, temperatures as high as  $10^8$  K (at a density up to  $10^{21}$  electrons  $\text{cm}^{-3}$ ) were reached, giving a strong continuum from the visible to the soft x-ray region.

I shall present only two examples:

(i) Neon resonance spectra<sup>19</sup> in the pure solid (*Figure 11*) exhibit the hydrogen-like series converging to  $E_G = 21.42$  eV, whereas the free atom ionization energy is 21.56 eV. This means that the Wannier exciton model is not really necessary for treating this very weak perturbation.

(ii) Effect of lattice cell size on the width. Generally the perturbation is strongest for large polarizability matrices, except when the cell size is too

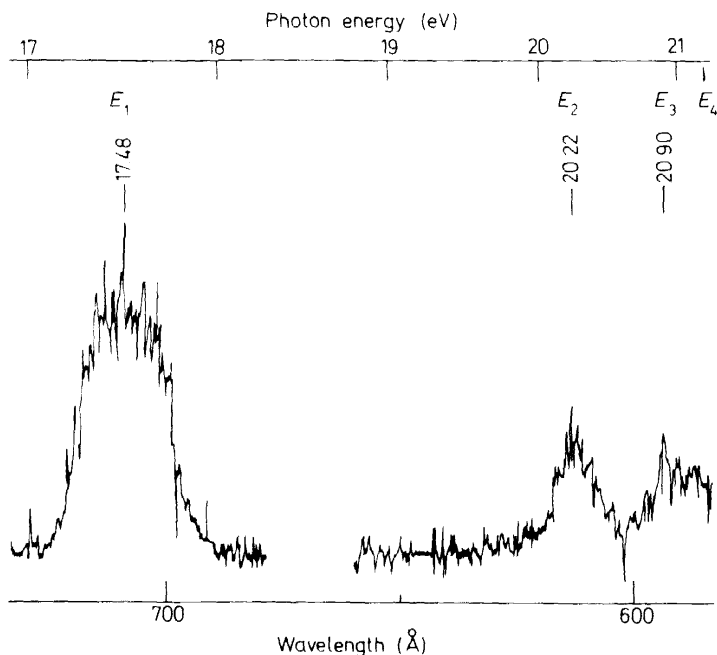


Figure 11. Absorption spectrum of solid neon in vacuum u.v.

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small with respect to the size of the orbitals involved in the transition. An interesting case is the  $B^2\Pi-X^2\Pi$  transition of NO, which is sharper in neon than in the other matrices. Furthermore there are extremely sharp bands in the neon matrix which constitute perhaps an excellent example of the Shpol'skii effect. I shall only show you briefly one spectrum obtained with a 10 m vacuum spectrograph of NO in solid neon at 4.2 K (*Figure 12*). Some phonon sidebands are visible; their half-widths are  $\sim 4\text{ cm}^{-1}$ .

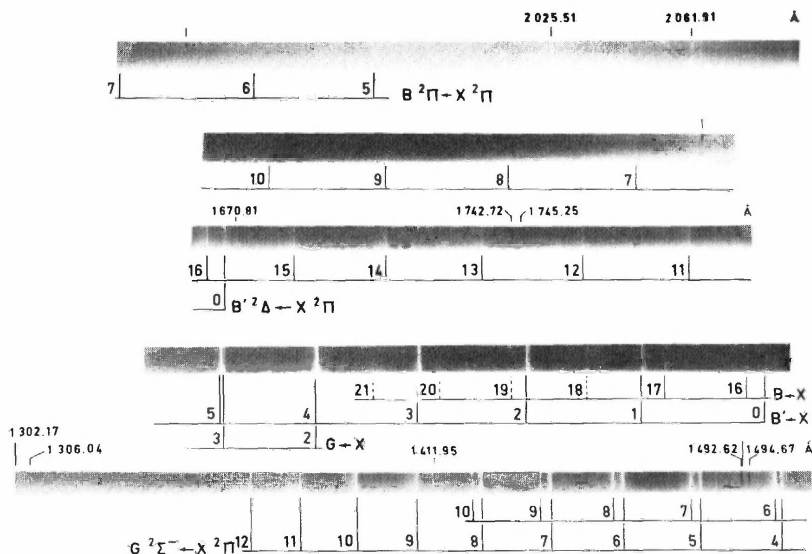


Figure 12. High-resolution absorption spectrum of the NO molecule trapped in a neon matrix, in vacuum u.v.

Let me close this part of my talk by saying a few words about the so-called satellite bands of atomic electronic transitions, which occur for example near the resonance lines of metal vapours when they undergo collisions with another atom.

The reason for mentioning this topic is that until now it seems that there was no generally accepted explanation for these satellites even at low pressures. Since they may occur in the matrix-isolated systems I believe it is appropriate to tell you about the recent result of Castex<sup>20, 21</sup>. She studied the xenon resonance lines in the vacuum u.v. spectrum, perturbed by various gases. Thus, because so far studies had been limited to metal vapours, difficult to handle, she obtained what we believe is the first quantitative information about the intensity of satellites, and also their dependence upon the temperature (*Figure 13*).

The results show that the logarithm of the integrated intensity is proportional to  $1/T$ . This points to the fact that the bands should be related to the bound Xe-Ar or Xe-Xe molecules, and not simply to the collisions. We do not know yet whether this experimental result is general, but it is in contradiction with several other theories.

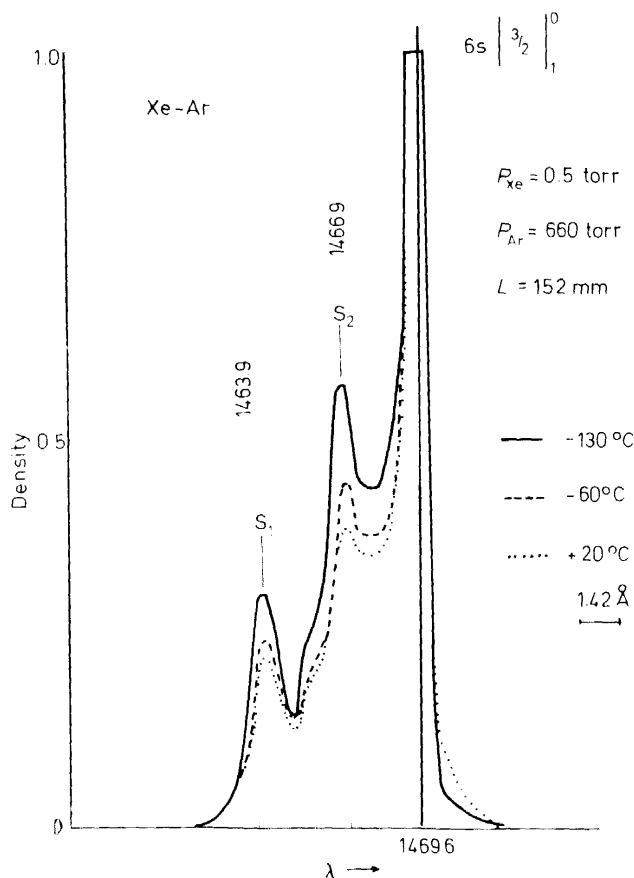


Figure 13. Temperature effect on satellites  $S_1$  and  $S_2$  of the xenon resonance line perturbed by argon gas

## CONCLUSIONS

(i) Phenomena occurring in the dense gas phase prefigure those occurring in the solid phase.

(ii) Matrix isolation is a different but equally useful tool: it allows the study of the interactions with highly excited states which exist, in equilibrium, only at very high temperatures.

(iii) Indeed particularly poorly known are the systems in which the electronic perturbations are strong, such as dense mercury vapour, where an insulator-metal transition occurs due to the proximity lowering of the ionization potential.

(iv) But even if one does not reach the range where drastic changes would occur, spectroscopic studies can lead to a better knowledge of the properties connected with the anharmonic properties and in general of the molecular interactions within a solid.

It is well known that under high pressure solids undergo phase transformations which are generally crystallographic in nature, tending to a dense packing, but are also electronic: when two atoms come closer, overlap forces and the Pauli principle determine a release of the bound electrons.

It is, in contrast, not so well known what happens when, starting with the density of a solid, one decreases the density gradually by raising the temperature under a sufficiently high pressure. One can expect in many cases a semi-conducting behaviour when the atoms are sufficiently widely spaced so that the conduction band is not formed.

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