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Luminescence spectra of matrix isolated N₂ at high pressure and low temperature

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N₂ molecules with a concentration of ca. 1% were isolated in Xe, Kr, and Ar. X-ray stimulated luminescence ($A \ ^3\Sigma_u^+ \rightarrow X \ ^1\Sigma_g^+$) was investigated as a function of pressure (<30 GPa), temperature (300 K and 77 K), and matrix material. Observed UV transitions were interpreted as rovibronic transitions of the impurity molecule along with phonon sidebands as lattice excitations. Spectra were analyzed due to band maxima of vibron progressions, bandwidth, and bandshape, Franck–Condon profiles, and molecule constants, each as a function of pressure. The main result was a shift of band maxima with pressure to lower energies at a rate of 100 cm⁻¹/GPa in Xe, 50 cm⁻¹/GPa in Kr, and 10 cm⁻¹/GPa in Ar. We modeled and explained these pressure-induced shifts of electronic bands by two mechanisms: a dielectric effect and a volume effect. © 1997 American Institute of Physics. [S0021-9606(97)00704-6]

INTRODUCTION

The technique of matrix isolation is applied successfully to almost any kind of spectroscopy and it deals either with physical or chemical oriented questions since it was developed in 1954.^{1,2} If a guest particle is isolated in the host matrix, the deformation of the first shell of neighboring rare-gas atoms is of the order of 1% or less compared to the undistorted configuration. This volume or cage effect is part of the contribution to the matrix shift, defined as $\Delta\nu_m = \nu_{mi} - \nu_{gas}$ and ν the energy of any kind of transition in the guest. If ultra high pressure (less than 10 GPa at $T < 20$ K) is applied, the crystal shrinks additionally and the lattice constant is reduced by 10%–30%. Since high pressure methods, especially the diamond anvil cell (DAC), are available (~1980) and are also successfully linked to almost any kind of spectroscopy^{3,4} it is straightforward to combine matrix isolation to high pressure techniques to raise the following questions:

(i) This type of condensed matter consisting of molecular crystals, mixtures, or diluted systems occurs in comets (Halley) or in moons of Uranus; it is challenging to model the IR spectra of these astrophysical objects by N₂, CO, ice, methane, etc.

(ii) Because it is feasible to now study individual particles in Paul-traps⁵ or detect the light of individual particles in solids,⁶ it might be interesting to study now quasi-free or matrix isolated molecules under extreme conditions such as ultra high pressure; then we expect the bondlength of the molecule to be changed remarkably by ca. 10⁻³.

(iii) Applying pressure will change the strength of guest–host interaction, because all the potential parameters, such as potential depth, equilibrium distance, and polarizability, are heavily pressure sensitive. In addition by varying pressure the interaction distance between lattice particles is altered and the potential will be tested on a larger scale and not only around the potential minimum.

(iv) Since the theoretical matrix shift $\Delta\nu_m$ consists of different contributions—such as electrostatic interaction, induction and dispersion, short range repulsion⁷—which are difficult to be determined by spectroscopy or scattering experiments, the additional pressure shift $\Delta\nu(p)$ by volume decrease will mainly help to get a deeper insight into this guest–host interaction.

Possible candidates which can easily be loaded into a DAC from respective gas mixtures are N₂, O₂, CO₂, CS₂, etc. in rare gases Ne, Ar, Kr, Xe. We expect forbidden rovibronic transitions to be partially allowed by pressure, that bending progressions are altered, etc. As a first example of a series of measurements of matrix isolated molecules at high pressure, we investigated the x-ray stimulated optical luminescence spectra of N₂ isolated in rare-gas matrices (Ar, Kr, Xe) at high pressure ($p < 30$ GPa) and varying temperature ($T = 77$ –300 K) in the region of the Vegard–Kaplan bands $A \ ^3\Sigma_u^+ \rightarrow X \ ^1\Sigma_g^+$. Characteristics of these rovibronic bands, such as band maxima, bandshapes, bandwidths, and intensities, are determined as a function of temperature, pressure, and matrix material. We will analyze these data due to standard methods of molecular spectroscopy and discuss them in

terms of pressure induced cage effect and matrix effects.

Considering published literature (~1970–1995) there are very few publications on matrix isolation at high pressure: IR studies up to 1.5 GPa at 5 K in H₂/rare-gas mixtures;⁸ Raman studies up to 1 GPa at 77 K in N₂/Ar mixtures;⁹ absorption measurements in Xe to determine the pressure dependence of the gap energy in the UV region;¹⁰ pressure dependent fluorescence investigations on Cr³⁺ ions in Al₂O₃;¹¹ Raman studies up to 40 GPa at room temperature on H₂ in He, Ne, Ar, and D₂;¹² synchrotron IR spectroscopy at megabar pressures in o/p hydrogen.¹³

EXPERIMENT AND RESULTS

Nitrogen and rare gases (Ar, Kr, Xe) of standard purity were premixed (0.5 to 1 bar N₂ and rare gas at final pressure of 60 bar) and the sealed DAC was loaded by use of a gas loading apparatus. Therefore, the concentration of matrix isolated molecules—due to partial pressure—was about 1% or less. The luminescence of N₂ molecules $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ was excited by x rays (Mo tube 50 kV, 55 mA) and analyzed by a computerized optical spectrometer. The local pressure was determined by the ruby fluorescence technique.¹⁴ In the case of low temperature investigations, the DAC was inserted in a liquid N₂ filled cryostat. Figure 1 shows typical spectra for N₂ in Xe. The rovibronic bands forbidden in the free molecule¹⁵ and partially allowed in the rare-gas matrices^{16–19} are shaded to lower energies.

Influence by pressure and temperature is distinctly recognizable. The band assignment is straightforward due to zero pressure measurements¹⁶ with the usual meaning: e.g., 0/5 means a transition within the N₂ molecule from an electronic excited level at vibrational ground state $A^3\Sigma_u^+(v'=0)$ to the electronic ground state at vibrational excited state $X^1\Sigma_g^+(v''=5)$. We studied several samples of N₂ in Xe, Kr, and Ar and obtained the following qualitative picture (Fig. 1): Band intensities of N₂ in Xe, Kr, and Ar decrease continuously by about 50% raising pressure. In Xe we observed stronger bands than in Kr and Ar, due to larger x-ray absorption; in Xe only these band intensities fade away at a characteristic pressure of ca. 15 GPa. The vibronic band maxima shift to lower energies with pressure $\Delta\nu/\Delta p \approx 100 \text{ cm}^{-1}/\text{GPa}$ in Xe, 50–60 cm⁻¹/GPa in Kr, and 10 cm⁻¹/GPa in Ar. In general and on the contrary, vibrational frequency shifts with pressure are to higher energies and of the order of 1 cm⁻¹/GPa for internal molecular modes and 10 cm⁻¹/GPa for molecular lattice modes. Since these energies for electronic transitions (~30 000 cm⁻¹), for vibron (~3000 cm⁻¹), and for lattice mode transitions (<100 cm⁻¹) are so different in size, it is more meaningful to compare here relative frequency shifts with pressure $(1/\nu_i)/(\Delta\nu_i/\Delta p)$. Considering in addition the influence of the different matrices on the isolated molecule via their compressibility β_T , we apply the concept of mode Grüneisenparameters $\gamma_i := (1/\beta_T \nu_i)/(\Delta\nu_i/\Delta p)$ and determine values between 10⁻² and 10⁻³. The bandshape of individual vibronic transitions resembles a symmetric Gaussian profile whose asymmetry parameter decreases slightly with pressure. Band widths de-

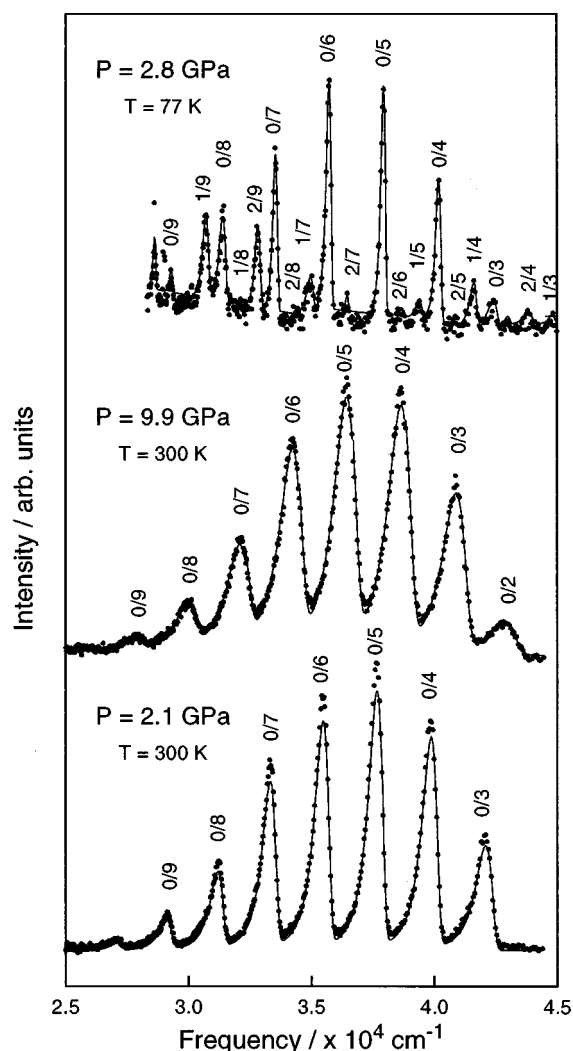


FIG. 1. Some luminescence spectra of N₂ in Xe at different pressures and temperatures are presented. These progressions belong to rovibronic transitions $A^3\Sigma_u^+(v'=0) \rightarrow X^1\Sigma_g^+(v'')$; the assignment 0/5 for example means an electronic transition from vibrational level $v'=0$ to $v''=5$.

crease by cooling and increase with pressure, as expected. The maximum of Franck–Condon profiles shifts slightly to higher energies with pressure in the case of N₂ in Xe and is almost unaffected in the case of N₂ in Kr and Ar. To model individual bands, shaded to smaller energies (see Fig. 1), we use either a pure mathematical fit procedure or a physical one based on combined bands consisting of a zero phonon line and a phonon sideband (see later).

DISCUSSION

First, we will describe the excitation mechanism after x-ray absorption; then we will analyze spectra with respect to band maxima, bandwidth, and shape, to discuss how molecule constants may change. Finally, we will model the frequency versus pressure shift to lower energies by two contributions: a decrease in volume and a change in dielectric properties as a function of pressure. But before this, we would like to repeat briefly what is known in the literature on

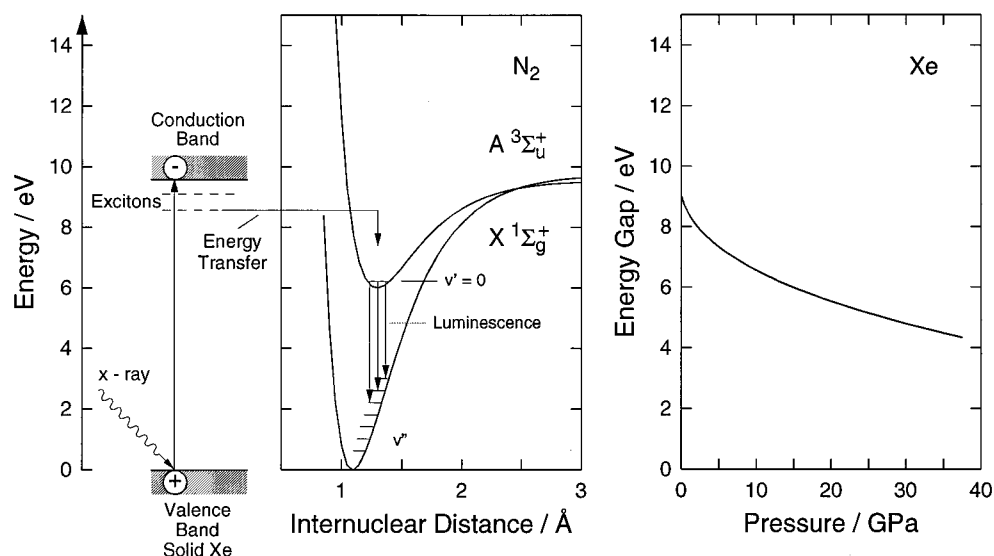


FIG. 2. Left part: Excitation mechanism (details see text, Discussion). Right part: Energy gap as a function of pressure in solid Xe.

vibrational relaxation in the $A\ ^3\Sigma_u^+$ state of N₂ in rare-gas matrices at low temperature and zero pressure.

Tinti and Robinson¹⁶ investigated x-ray stimulated luminescence of N₂ isolated in Ne, Ar, Kr, and Xe at $T=5$ K and zero pressure. They proposed an assignment of the Vegard–Kaplan band system ($A\rightarrow X$), determined molecular constants of matrix isolated in comparison to gas phase values, and studied in detail decay times of the vibrational relaxation in the $A\ ^3\Sigma_u^+$ state of N₂ ($\tau=0.4\text{--}3$ s.). Jodl and Bruno¹⁹ extended those investigations to different temperatures and to various N₂ concentrations. All individual bands show a distinct fine structure and temperature dependent bandwidth which was attributed to vibron–phonon coupling. The matrix-shift $\Delta\nu_m$ from experiment was explained by a theoretical model based on guest–host interaction due to combined Lennard–Jones type potential between the N-atom and rare-gas atom. Kühle *et al.*¹⁸ excited selectively individual electronic states $A\ ^3\Sigma_u^+$ of N₂ molecules embedded in Xe by synchrotron radiation and detected total luminescence. Systematic investigations of relative band intensities gave insight into competitive depopulation channels of excited levels like radiative or nonradiative vibrational relaxation and electronic energy transfer within N₂ aggregates. Pan *et al.*¹⁷ excited N₂ molecules isolated in Ne, Ar, and Kr matrices by an electron beam. All bands exhibit a doublet (spacing $35\text{--}70\text{ cm}^{-1}$) due to two distinct emitting crystal sites of the N₂ molecules in these matrices. By adding different further small molecules (CO, NO, etc.), a further relaxation channel of vibrational energy of N₂ molecules by energy transfer to suitable acceptors is opened, besides the one already known and described above.

Excitation mechanism and relaxation channels

X rays are absorbed by the rare-gas bulk material; more in Xe than Kr and Ar, due to the Z dependence of x-ray absorption. This behavior obviously explains why we observe a stronger N₂ luminescence in Xe than in Kr or Ar.

From the isolator conduction band the excitation energy is deposited into bulk exciton levels, lying at 8.4 eV for Xe, 10.0 eV for Kr, and 11.6 eV for Ar.²⁰ The isolated N₂ molecule is probably excited mainly by energy transfer from these lowest exciton bands (see Fig. 2). Then vibrational relaxation in the electronically excited state $A\ ^3\Sigma_u^+$ of N₂ molecules follows. At the end of this process, luminescence from the molecule is radiated within seconds, because these vibronic transitions $A\ ^3\Sigma_u^+(v'=0)\rightarrow X\ ^1\Sigma_g^+(v'')$, known as Vegard–Kaplan bands, are spin forbidden.

Now, if we apply pressure it is known that the band gap energy of the rare-gas matrix material is lowered (right part of Fig. 2 for Xe due to Refs. 10 and 21). If the exciton levels in Xe are lying below the pure electronic transition of the molecule (for N₂-gas at $p=0$ $T_{00}=6.2$ eV), no energy can be transferred from the matrix to the impurity and the total luminescence intensity will suddenly decrease. This happens here for Xe at $T=300$ K at about $p^*\sim 15$ GPa; due to Fig. 2 this means a gap energy at 6.0 eV. This formal difference in energies (T_{00} of N₂ at $p=0$ and E_{gap} of Xe at p^*) can be interpreted as a frequency shift to lower energies of $100\text{ cm}^{-1}/\text{GPa}$ in Xe (see discussion later). We observed this drastic decrease in intensity in Xe only, since our applied pressure range of less than 20 GPa was too small to lower also the band gap energy in Kr and Ar below the electronic transition T_{00} of N₂ molecule.

Cooling the sample to $T=77$ K, we observe a decrease in vibronic band width as expected (Fig. 1). In addition, we observe transitions from vibrational excited levels $A\ ^3\Sigma_u^+(v'=0,1,2)$ to $X\ ^1\Sigma_g^+(v'')$, so-called hot bands. Former investigations were performed at different lower temperatures with the following result: at $T=5$ K Tinti *et al.*¹⁶ observed transitions $A\ ^3\Sigma_u^+(v'=0\text{--}6)$ to $X\ ^1\Sigma_g^+(v''=7\text{--}15)$, at $T=77$ K Jodl *et al.*¹⁹ registered transitions $A\ ^3\Sigma_u^+(v'=0\text{--}3)$ to $X\ ^1\Sigma_g^+(v''=2\text{--}12)$, and in these experiments at $T=300$ K we assigned vibron bands

A ${}^3\Sigma_u^+(v'=0)$ to $X\ {}^1\Sigma_g^+(v''=2-9)$ only. Therefore, due to temperature there is a competition between two relaxation channels: radiative and nonradiative transitions. This last process, i.e., vibrational relaxation in the electronically excited state (vibrational energy in $\omega_e \sim 1460\text{ cm}^{-1}$ of N_2^*), must be much shorter than the radiative emission lifetime. The strong temperature dependence ($T=5\text{ K}$ to 300 K) favors a phonon assisted process [ω_D (rare-gas solids) ~ 45 to 65 cm^{-1}].

Further relaxation channels must be discussed but are improbable to our mind:

(i) Absorption of x-ray energy may dissociate N_2 molecules to produce N-atoms (energy at dissociation 9.8 eV)—or even N_2 -ions. We could not register any emission of N-atoms (known in literature¹⁶), which should be orders of magnitude weaker than this luminescence intensity of isolated N_2 molecules.

(ii) Traces of impurities may act as a quencher of this radiative emission: from electronically excited N_2 via electronic levels of impurity molecules (e.g., O_2 in the gas phase $T_{00}=4\text{ eV}$) or from vibrationally excited N_2 ($\Delta v''=2330\text{ cm}^{-1}$, $\Delta v'=1460\text{ cm}^{-1}$) to impurity vibrations (CO : $\Delta v''=2100\text{ cm}^{-1}$, O_2 : $\Delta v''=1550\text{ cm}^{-1}$, NO : $\Delta v''=1900\text{ cm}^{-1}$). Since we evacuated and purged the sample gas line, we expected impurities of this type to be less than 1%.

(iii) There is a certain possibility for depopulation of vibrational excitation in the A-state of the molecule via N_2 aggregates, if the concentration is high enough (few percent of N_2). Kühle *et al.*¹⁸ observed that relaxation takes place exclusively in steps of $\Delta v'=2$, seen in the intensity pattern, and this is strongly dependent on N_2 concentration. We observed a regular Frank–Condon pattern (see Fig. 1); consequently, we can assume a N_2 concentration of less than 1% and well separated matrix isolated molecules.

Frequency shifts by pressure and matrix material

Since the N_2 molecules are isolated in Xe, Kr, or Ar we can basically use the model of a simple harmonic oscillator in a cage along with the following three extensions: static relaxation of the molecular geometry at a substitutional site, modified dielectric properties due to the surrounding matrix, and dynamical coupling of the oscillator motion to the phonon bath due to temperature. Therefore, it is straightforward to evaluate the luminescence spectra (Fig. 1) according to principles of molecular physics.

After assignment ($A\ {}^3\Sigma_u^+(v'=0) \rightarrow X\ {}^1\Sigma_g^+(v''=1-9)$) we can plot the maxima of vibron bands versus pressure (Fig. 3) and use a polynom for fitting

$$\nu_{\text{RGS}}(p)|_{T=300\text{ K}} = \nu_0(p=0) + \frac{\Delta\nu}{\Delta p} p + O(p^2).$$

The justification for this parabolic fitting is given by Lin,²² one of the very few publications on that matter. The theoretical model by Lin²² predicts that the pressure induced frequency shifts of vibronic bands are the same; the pressure dependence of the frequency shifts is in general parabolic, sometimes linear. But he considered only the “volume

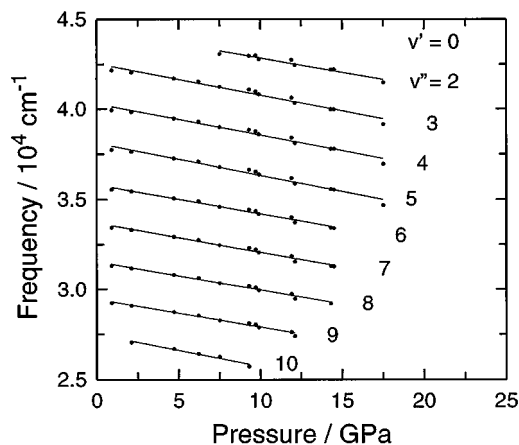


FIG. 3. Band maxima (in cm^{-1}) of luminescence spectra as a function of pressure (in GPa) for N_2 in Xe at $T=300\text{ K}$ (notation 0/5, for example, as in Fig. 1; the solid lines serve as guide for the eye).

term” such that addition of external pressure will displace nuclear coordinates; if this displacement is negative (positive) with pressure one observes a shift to smaller (larger) energies. Of course we know the matrix lattice is contracted by pressure; but we can neither estimate the cage volume (N_2 molecule on a substitutional site of rare gas matrix), nor the change of bondlength during the vibronic transition of the matrix isolated molecule affected by pressure. So Lin’s model²² is not directly applicable here.

The extrapolated frequency values of the N_2 luminescence in Xe, Kr, and Ar to zero pressure values at $T=300\text{ K}$ agree well with data from literature at $T=77\text{ K}$ ¹⁹ and at $T=5\text{ K}$ ¹⁶ within instrumental error and frequency shift by different temperatures. The slopes $\Delta\nu/\Delta p$ are the same for different vibronic bands and are approximately $-100\text{ cm}^{-1}/\text{GPa}$ for Xe, -50 for Kr, and -10 for Ar (see Fig. 3). Only in Xe matrices do we observe a small parabolic behavior of all bands according to $d^2\nu/dp^2=8\text{ cm}^{-1}/\text{GPa}^2$. This relative frequency shift $(1/\nu) \cdot (\Delta\nu/\Delta p)$ (not directly identical to mode Grüneisenparameters) is exploitable for further considerations only, especially in size and sign. Their relative vibronic shifts at frequency of $\sim 40\,000\text{ cm}^{-1}$ are of the order of -10^{-4} GPa^{-1} , whereas vibrational shifts at frequencies of $\sim 2000\text{ cm}^{-1}$ deliver values like $+10^{-3}\text{ GPa}^{-1}$ and shifts for phonon excitations ($\sim 100\text{ cm}^{-1}$) $+10^{-1}\text{ GPa}^{-1}$. The positive frequency shifts of the last two kinds of excitations are qualitatively explainable in simple mass-spring model in which relevant energy levels of an oscillator are shifted to higher energies by pressure. This negative frequency shift in the case of vibronic excitations means that each vibronic level is changed individually by pressure such that the difference between excited state and ground state of matrix isolated N_2 is getting smaller.

Before trying to find a suited model to explain this red shift of luminescence maxima in Xe, Kr, and Ar, we may compare first these shifts in size and sign to other pressure dependent parameters to realize the correct dependence in the model. The ratio of these frequency shifts ($\text{cm}^{-1}/\text{GPa}$) is

(−100):(−50):(−10) for Xe, Kr, and Ar, respectively. If we do not consider the cage, i.e., the first shell of matrix atoms around a N₂ molecule, but only the bulk behavior with pressure in the quasi-harmonic approximation ($\nu \propto V^{-\gamma}$), we can explain the red frequency shift by a volume decrease if we raise pressure $\Delta\nu/\Delta p \propto -\Delta V \propto \beta_T$. Now, comparing the different rare-gas solids via the isothermal compressibility β_T (GPa^{−1}), we get 0.27:0.29:0.34 for Xe, Kr, and Ar,²³ which conducts to a reverse order from Xe to Ar. Therefore, this red shift cannot merely be explained by a bulk term, describing the compressed bulk material. A second term for comparison may be the matrix-shift, $\Delta\nu_m = \nu_{\text{Solid}} - \nu_{\text{gas}}$ of the pure electronic transition of the N₂ molecule at $p=0$ and $T=5$ K [$A^3\Sigma_u^+(v'=0) \rightarrow X^1\Sigma_g^+(v''=0)$]. The ratio of matrix shifts (cm^{−1}) are (−342):(−238):(−131) in Xe, Kr, and Ar,¹⁹ showing the right size and trend as the pressure induced frequency shift of luminescence maxima. This matrix shift in general is formed by several parameters like the potential parameters of the free and isolated molecule (Lennard–Jones type of potential ϵ, σ) and the interaction of impurity with matrix described by dielectric parameters. Therefore, we suggest a third comparison via polarizability. The ratio of the bulk polarizabilities are 4.0:2.5:1.6 of Xe, Kr, and Ar.²⁴ Consequently the trend Xe, Kr, and Ar via matrix shift and polarizability are the same.

Bandshapes and bandwidth

Each vibron band of N₂ luminescence in Xe, Kr, and Ar at room temperature and small pressure is strongly asymmetric as measured from band maximum toward lower energies to be 750–900 cm^{−1} in comparison to bandwidth (~600 cm^{−1}) and resolution (~200–300 cm^{−1}) (see Fig. 1). Cooling the sample to $T=77$ K this red tail and the bandwidth decreased by a factor of 3 roughly; a general trend as we expected. Raising pressure within cell this asymmetry decreased clearly in Xe by a factor of 2, whereas in Kr it looks to be constant and in Ar we observed a slight increase, whereas bandwidths of vibron bands increased linearly with pressure in all matrices (see Fig. 4).

To perform a more quantitative analysis for physical interpretation of this asymmetry in bandshape we considered two kinds of fit procedures:

(i) All bands in one spectrum were fitted by one asymmetry parameter (of course, in addition, background and slope) by individual asymmetric Gauss-fit functions. The justification for this physical model is twofold: this fit procedure is usually applied and well tested in pressure dependent luminescence studies of semiconductors. On the other hand, Lin²² derived bandshape functions of vibronic bands in absorption and emission for molecular crystals, which are described by an asymmetric Gaussian function.

(ii) Each individual vibron band is modeled by one Gaussian profile as the zero phonon line (pure vibronic transition within molecule) and another Gaussian at the lower energetic side in spectrum as the phonon sideband. By this combination band we can model the relaxation of the matrix material to an electronic transition of the impurity molecule.

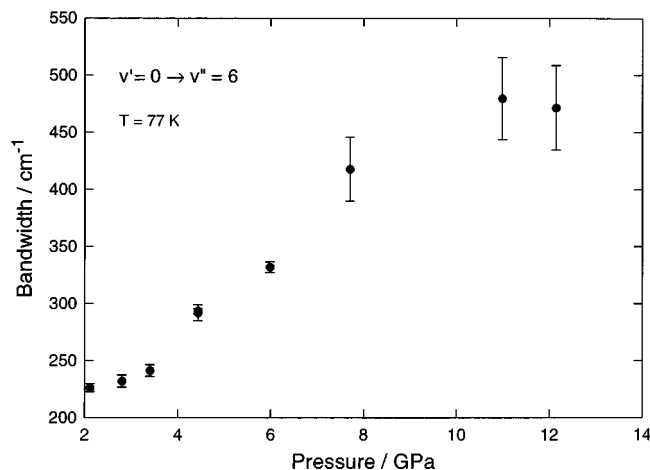


FIG. 4. Bandwidth as a function of pressure for one specific transition as an example: N₂ [$A^3\Sigma_u^+(v'=0) \rightarrow X^1\Sigma_g^+(v''=6)$] in Xe at $T=77$ K. At small pressure resolution is limited by bandpass of monochromator because of weak signal; at high pressure bands are broadened and deconvolution into individual bands is problematic.

This dynamic interaction must obviously be temperature and pressure dependent. (For general purposes see Ref. 25).

The justification for this second model (ii) is as follows: In emission these so-called Vegard–Kaplan bands show a red tail^{16,19} as in our spectra; in absorption this phonon sideband must be situated at the higher energetic side of the zero phonon line.¹⁸ The spacing ΔE between the maxima of these two Gaussian bands in one vibronic transition [$A^3\Sigma_u^+(v'=0) \rightarrow X^1\Sigma_g^+(v'')$] is about 350 cm^{−1} at $T=300$ K ($kT=210$ cm^{−1}) and 120 cm^{−1} at 77 K ($kT=60$ cm^{−1}), which means $\Delta E \sim 2kT$. Considering a Debye frequency for matrix material of about 50 cm^{−1}, about <10 bath phonons are excited during the relaxation of the bulk to a pure electronic transition in the impurity. For comparison the nonradiative vibrational transition in the $A^3\Sigma_u^+$ state ($\Delta\nu'=1460$ cm^{−1}) requires about 30 bath phonons. The bandwidth of this phonon sideband is (at low pressures) about 800 cm^{−1} at 300 K and 400 cm^{−1} at 77 K. Due to the relaxation process one has to sum up and weigh according to sample temperature the multi-phonon density of states leading to such broad features. This deconvolution of one asymmetric band into two Gaussian curves delivers the bandwidth of zero phonon line and phonon sideband which are reasonable in size and variation with pressure (see later). In Xe we stated a decrease in asymmetry parameter with pressure. Since all features broaden by pressure—the zero phonon line due to pressure inhomogeneities and the phonon sideband due to pressure dependence—details of the fit function are smeared out. Due to literature similar values at zero pressure are as follows: Tinti *et al.*¹⁶ report a red tail 300–400 cm^{−1} in emission at 5 K and Kühle *et al.*¹⁸ a blue tail 150–200 cm^{−1} in absorption at 7 K. The bandwidth of zero phonon line is reported to be ~40 cm^{−1} by both authors. Kühle *et al.*¹⁸ determined a Huang–Rhys factor to describe this electron–phonon coupling (see for instructions also Ref. 25): they found a medium size electron–phonon coupling strength from intensity

ratios in spectra and they modeled the bandwidth of sideband feature by 4–5 bath phonons with an average bath phonon of $\sim 32 \text{ cm}^{-1}$ at $T=5 \text{ K}$.

Since electron–phonon coupling is much stronger than phonon–phonon coupling, in principle, this gives rise to multi-phonon excitations. Consequently, bandwidth and phonon sideband are much broader than in pure vibrational transitions: here bandwidth of vibronic transition $\sim 30 \text{ cm}^{-1}$, whereas bandwidth of pure vibration $< 0.1 \text{ cm}^{-1}$.²⁶

Other possibilities to describe this asymmetry in vibronic bands are briefly discussed now: (i) polymer features next to monomer transitions (spacing $< 1 \text{ cm}^{-1}$) are reported by Kieffe *et al.*²⁷ for N₂ in Ar and (ii) transitions from $v' > 0$ levels, observed at $T=77 \text{ K}$ (see Fig. 1), may also be possible, at $T=300 \text{ K}$. These hot bands, lying close to $v'=0$ transitions, are much weaker in intensity and may mislead to asymmetry. But due to Fig. 1 this may be an explanation for the $v'=0$ to $v''=7$ asymmetry (sum of $v'=0$ to $v''=7$ and $v'=2$ to $v''=9$ transitions); but there is no counterpart $v' > 0$ to v'' for the $v'=0$ to $v''=5$ transition. (iii) Since N₂ molecules may rotate in the matrix cage, we can apply the well known rotor model too. Due to temperature and selection rules we expect *P* and *R* branches which are symmetric to the *Q_J* branch (here called zero phonon line) delivering a bandwidth of $150\text{--}200 \text{ cm}^{-1}$ at rotations $J=10$ to 12 . (iv) Since this asymmetry is clearly temperature and pressure dependent, as described above, we cannot justify this by inhomogeneous broadening. Part of the ZPL is certainly inhomogeneous due to crystal quality and local stress. (v) In literature about matrix isolated molecules, site splitting of vibron transition are reported to be $\sim 40 \text{ cm}^{-1}$ (mainly in Ar matrices).

From our spectra extrapolated to zero pressure, we can extract the temperature dependence of vibron bandwidth to be $400\text{--}500 \text{ cm}^{-1}$ at 300 K and $\sim 200 \text{ cm}^{-1}$ at 77 K (Fig. 4). In combination with data from literature, such as $\Gamma(T=5 \text{ K}) \sim 30 \text{ cm}^{-1}$ in emission¹⁹ and $\Gamma(T=7 \text{ K}) \sim 40 \text{ cm}^{-1}$ in absorption,¹⁸ these values at three different temperatures follow a linear relation. Since bandwidth is directly related to phonon occupation number,²⁶ $\Gamma(T) \propto n(T, \omega)$ is proportional to T in the high temperature case. Similarly bandwidth of phonon sideband evolves: $\Gamma(T=5 \text{ K}) \sim 160 \text{ cm}^{-1}$,¹⁹ $\Gamma(T=77 \text{ K}) \sim 200 \text{ cm}^{-1}$, and $\Gamma(T=300 \text{ K}) \sim 300 \text{ cm}^{-1}$.

All bandwidth at a given temperature broaden due to pressure, as presented in Fig. 4 for Xe at 77 K . The error is pretty large, since the luminescence signal was weak and deconvolution into two Gaussian profiles produced some uncertainty. Nevertheless, this linear increase of bandwidth with pressure can be explained analog to considerations of broadening of bandwidth in NaNO₃²⁸ briefly as follows: by pressure the phonon density of states will be broadened, therefore more transitions in this combination band (vibron and bath phonon) are accessible, lowering lifetime or broadening bandwidth of this specific transition, as expected.

Change in molecule constants by pressure

Since matrix isolated nitrogen molecule can be treated as an anharmonic oscillator we can deduce molecule

constants—such as fundamental frequency ω_0 (or ω_{Raman}), anharmonicity $\omega_e x_e$ and Franck–Condon factors—from vibronic spectra in a straightforward manner. Variation of cage diameter (N₂ on a substitutional site), of potential parameter by matrix material (Xe, Kr, and Ar), and by pressure may also alter these molecule constants. Comparing those to gas data, to pure solid N₂ data, and to data of N₂ in Xe, Kr, and Ar at $p=0$, we may reach more insight on how the free molecule has to be changed in a compressed bulk material.

Unfortunately, these derived molecule constants from our spectra exhibit large errors and uncertainties: e.g., we find ω_0 and $\omega_e x_e$ from differences in band frequencies, values which scatter already appreciably (Fig. 3). Finally, sometimes we can use all data together (8 samples, 150 spectra) or sometimes we can choose one set only. The transmission from diamonds in the DAC changes from one to other experiment and due to applied pressure; as a consequence $\Delta I \sim 10\%$.

If we plot the difference in band frequencies ΔG from $v'=0$ to v'' transitions as a function of vibrational quantum numbers for a given pressure, we can derive ω_0 from intersection and $\omega_e x_e$ from the slope [Fig. 5(a)]; from differences of hot bands $v'=0, 1, 2$ to $v''=\text{const.}$ we also get analog molecule constants for the electronically excited state ($A^3\Sigma_u^+$). Performing this procedure for several pressures, we can plot $\omega_0(p)$ and $\omega_e x_e(p)$.

The pressure dependence of the fundamental mode of N₂ in the Xe matrix behaves like the one of pure solid N₂, as a general trend [Fig. 5(b)]. The error bars increase substantially, because vibron bands broaden and decrease in intensity raising pressure. For Xe at $T=77 \text{ K}$ and $p=2.8 \text{ GPa}$ the fundamental mode of the N₂ molecule in the electronically excited state is $1431 \pm 5 \text{ cm}^{-1}$ ($\sim 1420 \text{ cm}^{-1}$ at $p=0$), whereas the gas phase value is reported to be $1453 \pm 0.8 \text{ cm}^{-1}$.¹⁶ It seems to be that the *A* state of matrix isolated N₂ is more perturbed by the matrix under pressure than the ground state $X^1\Sigma_g^+$.

In Fig. 5(c) we present the anharmonicity $\omega_e x_e$ of N₂ ($X^1\Sigma_g^+$) in Xe, giving the right size as in the gas phase or matrix isolated case at zero pressure. Because their values are too uncertain at higher pressure, we cannot decide about an increase or decrease of molecule anharmonicity with pressure. From overtone band differences in the $A^3\Sigma_u^+$ state (such as $v'=0$ to $v''=4$ and $v'=2$ to $v''=4$) in comparison to fundamental band differences (such as $v'=0$ to $v''=4$ and $v'=1$ to $v''=4$) we can determine the anharmonicity in the electronically excited state $\omega_e x_e^* \sim 10^2 \text{ cm}^{-1}$ which is much larger than $\omega_e x_e^* = 14.02 \text{ cm}^{-1}$ in the gas phase.¹⁶ This might be a further hint that the excited state $A^3\Sigma_u^+$ of matrix isolated N₂ is much more perturbed than the ground state $X^1\Sigma_g^+$ at elevated pressure.

In general, from Franck–Condon factors (intensity distribution Fig. 1) and from their change with applied pressure, one can estimate how much the two potential curves $A^3\Sigma_u^+$ and $X^1\Sigma_g^+$ are shifted relative to each other in molecule bondlength, varying matrix material and pressure. In Xe for example the maximum of this vibron progression is slightly shifted from $v'=0$ to $v''=5$ at $p=2.1 \text{ GPa}$ to $v'=0$ to $v''=4$

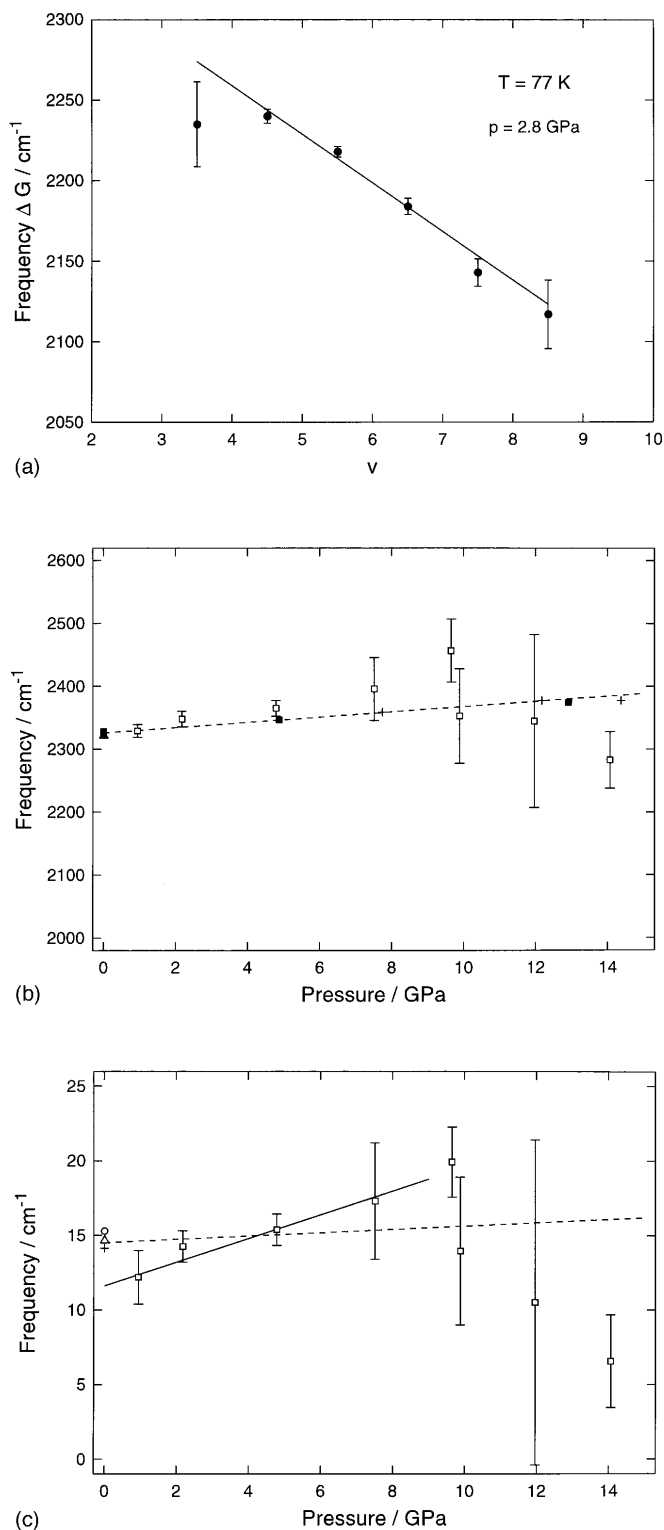


FIG. 5. Molecular constants of N₂ in Xe as a function of pressure. (a). Difference in band frequencies as a function of vibrational quantum number (details see text). (b). The fundamental mode of N₂, gained by extrapolation of (a), in Xe as a function of pressure. Some literature values for comparison: \blacktriangle zero pressure values,²⁹ extrapolated to room temperature from $\omega(T)$ studies; $+$ pure N₂ at $T=300 \text{ K}$ by Raman studies³⁰ and \blacksquare pure N₂ at $T=300 \text{ K}$ by Raman studies.³¹ Above 8 GPa the error in our values increases, because we determined this Raman frequency indirectly from these luminescence spectra. (c). Molecule anharmonicity $\omega_e x_e$ as a function of pressure and in addition gas phase value ($+$), N₂ in Xe (Δ) and N₂ in Ar (\circ) at $p=0$ by Ref. 16.

at $p=9.96 \text{ GPa}$; i.e., the minimum of one potential curve with respect to the other is shifted to larger bondlength ($\Delta r \sim +5\%$).

Finally, well known selection rules for vibronic transitions due to symmetry of vibrational states ($v'=1,2$ to v'' gerade or ungerade) are well reproduced by our investigations (Fig. 1), spectra at 77 K and spectra by Ref. 16; check for example the missing $v'=1$ to $v''=6$ transition. Maybe applied pressure on matrix material was not large enough to brake the symmetry in molecule transitions as hoped.

The conclusive observation is that, due to measured molecule constants from our spectra, despite the large uncertainties, we can derive a trend such that the electronically excited state $A^3\Sigma_u^+$ of N₂ in Xe is more perturbed than the ground state $X^1\Sigma_g^+$ at elevated pressure ($p < 20 \text{ GPa}$); the ground state of matrix isolated N₂ behaves like pure solid pressurized N₂.

Frequency shifts: application of Drude–MSA– $p\Delta V$ model of Agnew and Swanson

Pressure induced shifts of electronic bands of an isolated molecule in a host material have been traditionally explained by two mechanisms: a dielectric effect, i.e., a perturbation of the molecule's transition dipole due to the density-driven change in the dielectric properties of the surrounding material, and a volume effect, i.e., the coupling to the external pressure of the volume change between two electronic states of the molecule.

After recognizing that neither of the two effects can completely explain all the available data, Agnew and Swanson³² have proposed a model which incorporates both. In their approach, the volume term accounts for short-range repulsive effects, while the dielectric term accounts for long-range dispersive effects. This latter term is modeled after the quantum statistical treatment of Schweizer and Chandler^{33,34} in the mean spherical approximation (MSA) with molecular dipoles being represented by Drude oscillators. With an appropriate choice of the few parameters involved, this "Drude–MSA– $p\Delta V$ " model has been able to reproduce a number of experimental observations.³²

Although the Agnew–Swanson (A–S) model was originally developed for absorption bands in liquids, we found it interesting to try to extend its application to the present case of luminescence bands in crystals. In fact, pressure shifts of N₂ bands in rare gases appear to consist of both a dielectric and a volume contribution. The observed negative (red) shift with negative slope with respect to pressure, and a nonzero value at zero pressure, is a strong indication of a dielectric effect (positive shifts are predicted only for the rather unusual case of an impurity transition at a higher energy than the matrix typical frequency). The approximate scaling of the matrix ($p=0$) shift with the matrix polarizability (see above) is also consistent with dielectric models.³² On the other side, a $p\Delta V$ term is expected to better reproduce the pressure dependence of the shift, which is almost perfectly linear.

In the A–S model, the pressure dependence of the electronic transition frequency ν of an impurity i in a host ma-

TABLE I. Agnew–Swanson model parameters for N₂ in rare-gas matrices (ν/cm^{-1} , $\alpha/\text{\AA}^3$, $\sigma/\text{\AA}^3$, $\Delta V/\text{\AA}^3$).

		ν_i^a	α_i (Ref. 38)		
N ₂		38 408	1.76		
RGM	ν_0 (Ref. 33)	α_0 (Ref. 24)	$\sigma(p=0)^b$	σ^b	ΔV
Xe	97 835	4.0	4.50	4.4:3.7	-2.5
Kr	112 912	2.5	4.18	4.0:3.3	-0.5
Ar	127 108	1.6	3.95	3.5:3.1	0

^aPresent work, 0/4 transition.^bSee the text for a discussion of σ values.

terial is given by $\nu(p) = \nu(p=0) + p\Delta V + \Delta\nu(\nu_i, \alpha_i, \nu_0, \alpha_0, \sigma, \rho(p))$ (Ref. 32) where $p\Delta V$ is the volume term, $\Delta\nu$ is the polarization (dielectric) term, and the parameters on which $\Delta\nu$ depends are defined as follows: ν_i, ν_0 are the impurity and matrix frequency, respectively, α_i, α_0 are the impurity and matrix polarizability, and σ is the hard shell diameter of both the impurity and the matrix molecules.

The polarization term also depends on the number density $\rho(p)$ of the matrix. In our implementation of the model, density values for the observed pressures were derived through a Birch–Murnaghan equation of state,³⁵ which fits Xe data at $T=0$ and $p=2.40$ GPa. The T -dependent contribution can be calculated in the Mie–Grüneisen and Debye approximations.³⁵ An equally good fit to pV data of Ar (and also of Xe) in the same pressure range can be obtained using molar volume (V_0) and bulk modulus (B_0) values obtained by piston displacement techniques.³⁶ Values reported in the same work were used in the case of Kr, for which no pV data are available above 2 GPa.

Parameters used in our calculation for the 0/4 transition are reported in Table I. Experimental values were used for ν_i , α_i , and α_0 . The Drude oscillator frequency ν_0 was set equal to the ionization energy of the matrix material.³³ The value of σ for Xe, Kr, and Ar was initially chosen as to give the best fit to the $p=0$ shifts. These values (Table I) are in good agreement with nearest neighbor distances in the lattice, even though the corresponding reduced density $\rho\sigma^3$ is about 10% above the theoretical value for a close-packed structure ($\sqrt{2}$). In the pressure range of our experiments, density increases by more than a factor of 2, and it seems unrealistic to let the reduced density increase of the same factor. Consequently, the value of σ was varied with density such that $\rho\sigma^3$ was fixed at the $p=0$ value for each element. This procedure was used in other implementations of the Drude–MSA model.^{32,35}

To check the validity and consistency of parameters α_0 , σ , and ρ , we calculated the dielectric constant of the matrix material following the classical treatment for nonpolar fluids in the MSA approximation.³⁷ With our values of α_0 and of $\sigma(\rho)$, curves are obtained for $\epsilon(\rho)$ which are in very good agreement with dielectric constant measurements on the pure rare-gas solids.^{34,40–42}

Finally, the parameter ΔV was adjusted to fit our spectroscopic data. A negative ΔV was found, decreasing in absolute value in the series Xe, Kr, Ar, with a null value for Ar (Table I). Some of the resulting functions are plotted: Fig. 6

shows as an example for the 0/4 transition the influence of both contributions to the matrix shift; whereas in Fig. 7 the experimental frequency shift of the N₂ transition in Xe (symbols) is compared to the theoretical values due to this model (straight lines).

Although, in principle, it should represent the volume change between the excited and ground state of the molecule, the parameter ΔV has no simple physical interpretation. It has been observed that this effect involves the volume of the complex molecule solvent, rather than that of the molecule alone.³² In fact, if nitrogen alone were to be considered, an increase in volume would be expected (see Fig. 2). Furthermore, a different ΔV for the three matrix materials would be difficult to explain. According to the proposed excitation and relaxation mechanisms, the excited state is in equilibrium. Thus, in our opinion, our results indicate that the equilibrium value of the N₂-matrix cage diameter is smaller for the excited state than for the ground state, in analogy with what has been suggested for benzene in propane.⁴³ This is consistent with a softening of the repulsive potential in the excited state, which, according to ΔV values, is most effective in Xe, while it is absent in Ar. Actually, the interaction with the excited N₂ state is maximum for Xe, as

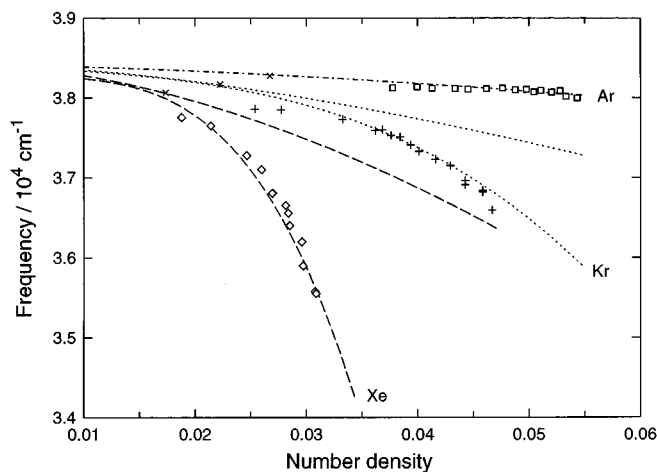


FIG. 6. Frequency shift (cm^{-1}) of N₂ 0/4 transition in rare-gas matrices, calculated with the Agnew–Swanson model as a function of number density ρ [\AA^{-3}]: curves: dashed, Xe; dotted, Kr; dash-dot, Ar. For each matrix, the lower curve is the total frequency, while the upper curve is the polarization effect alone ($\Delta V=0$). Experimental points: \diamond , Xe; $+$, Kr; \square , Ar; \times , matrix shift ($p=0$) for Xe, Kr, Ar in order of increasing density.

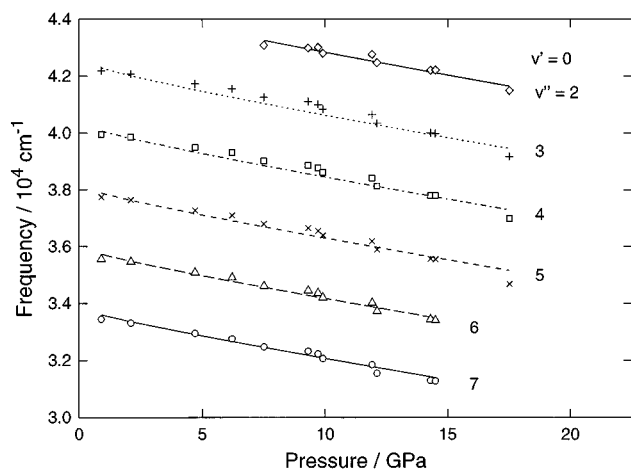


FIG. 7. Frequency shift of N₂ ($v'=0$, $v''=2, \dots, 7$) transition in Xe, calculated with the Agnew-Swanson model as a function of pressure.

is shown also by the magnitude of the change in the vibrational frequency with respect to the gas phase (see Table I).

CONCLUSION

Our general aim was to combine the technique of matrix isolation with high pressures; the specific task was to study N₂ molecules isolated in Xe, Kr, and Ar under extreme conditions, i.e., pressure at several GPa and low temperature. The diamond anvil cell was loaded with a gas mixture. We excited luminescence of Vegard-Kaplan bands in N₂ molecules by x rays and analyzed rovibronic transitions $A^3\Sigma_u^+(v'=0) \rightarrow X^1\Sigma_g^+(v'')$ as a function of pressure, temperature, and matrix material.

The excitation of the electronically excited N₂ is achieved by x-ray absorption of the bulk material and energy transfer via bulk excitons. The transition to the ground state of the impurity molecule embedded in a rare-gas matrix is possible through different relaxation channels, radiative or nonradiative. We consider this excitation model to be correct because if we apply pressure the UV energy gap in Xe is lowered below the pure electronic transition ($A \rightarrow X$) in N₂ and the luminescence signal disappeared at a critical pressure.

We discussed the characteristics of these rovibronic spectra, such as bandwidth, bandshape, Franck-Condon intensity distributions, term values, in the model of an anharmonic oscillator embedded in a solid with static and dynamic coupling between nitrogen atom and rare-gas atom. Of interest is the large pressure induced frequency shift of band maxima to lower energies of N₂ molecule luminescence matrix isolated in rare-gas solids. Comparing qualitatively this energy shift by pressure in Xe to Kr to Ar, we found this trend again confirmed in the different respective matrix-shifts [i.e., pure electronic transition of N₂ ($A \rightarrow X$) in Xe, Kr, and Ar in comparison to gas phase values]. Comparing this energy shift to simple solid parameters of matrix mate-

rial, such as lattice constant or compressibility, could not describe the expected trend.

A quantitative model to describe the pressure induced frequency shift of band maxima must contain therefore two terms: a dielectric term and a volume term. The coincidence between measured values and theory is very satisfying; all model parameters necessary for this fit procedure, such as ionization energy and polarizability of N₂ molecule and of Xe, Kr, and Ar and hard shell diameter (equivalent to impurity cage), are altogether realistic with respect to literature data.

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