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Electronic band gap, excitonic binding energy, and electron-hole exchange energy of KI under high pressure

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In this paper we investigate the electronic (excitonic) energy levels in KI under hydrostatic pressure using multiphoton excitation. The technique of three-photon absorption spectroscopy was used to find the pressure dependence of the $n=2$ exciton polariton and the nominally forbidden $F=2$ paraexciton. These data enable us to calculate the pressure dependence of the band gap, the excitonic binding energy, and of the electron-hole exchange energy for KI.

I. INTRODUCTION

Many important properties of solids depend on their electronic structure, among them their behavior as metals or insulators and the way in which they interact with light. The electronic energy levels of crystals depend on the distance between neighboring atoms, molecules, or ions, in extreme cases permitting materials to make transitions between insulating and metallic behavior depending on these distances. Probably the least complex way to change the lattice constant is by using hydrostatic pressure. The energy levels can then be probed using light which will couple with optically allowed transitions to form polaritons, such as the so-called exciton polaritons in the case of electron-hole pairs below the band gap. Since the band gaps of many interesting substances such as alkali halide crystals are beyond the easily accessible single-photon tuning range of a dye laser, multiphoton spectroscopy can provide a useful alternative to excite those energy levels and even others that are actually symmetry forbidden for one-photon transitions.[1] Alkali halide crystals have band gaps ranging from 5 to 10 eV and very high one-photon absorption coefficients.[2] Therefore, measurements of the band gap and its pressure behavior would require uv/vuv (vacuum ultraviolet) one-photon excitation and very thin samples making surface effects and strain dominating influences on these samples. In multiphoton spectroscopy, on the other hand, the light interacts very weakly with the solid where the process is a bulk effect and probes the whole crystal.

KI was chosen as a test case of the applicability of these techniques to samples at high pressures. Figure 1 shows the polariton dispersion relations for KI near the center of the Brillouin zone for the energy region from the lowest triplet exciton with energy E_P, to the band gap with energy E_G. The dashed lines correspond to the excitonic energies E_{nT} when there is no interaction with light ($E_{1T}, E_{2T}, E_{3T}, \ldots$)—the so-called transverse energies—and the longitudinal energies E_{nL} with $n=1,2,3,\ldots$ that arise from the coupling of the excitons with the electromagnetic field. The excitons can couple to light because they are singlet-triplet-mixed states of symmetry Γ_4^-, with a total angular momentum of $F=1$ (the conduction-band electron has a symmetry of Γ_6^+ and the valence-band hole a symmetry of Γ_8^-). The pure triplet paraexciton ($F=2$) has a symmetry of $\Gamma_5^- \oplus \Gamma_3^-$ and the three-photon excitation of it would be symmetry allowed, but spin forbidden. However, this last rule could be relaxed somewhat and interaction with light could be allowed because the finite optical wave vector mixes the $F=1$ and $F=2$ exciton states.[3,4] In part because the photons we are using interact only weakly with the crystal, the momentum remains a well-defined quantity.

Recently we reported the use of three-photon absorption spectroscopy to investigate the $n=1$ exciton-polariton structure of KI under hydrostatic high pressure.[5] The dotted points in Fig. 1 show excitations that might be observed with three-photon spectroscopy in a simple forward geometry. Those with a wave vector $k \approx 5.1 \times 10^7\ \mathrm{m}^{-1}$ correspond to three polaritons each with about $1.7 \times 10^7\ \mathrm{m}^{-1}$ and energy $E/3$ fusing together in the forward direction—called transverse polaritons

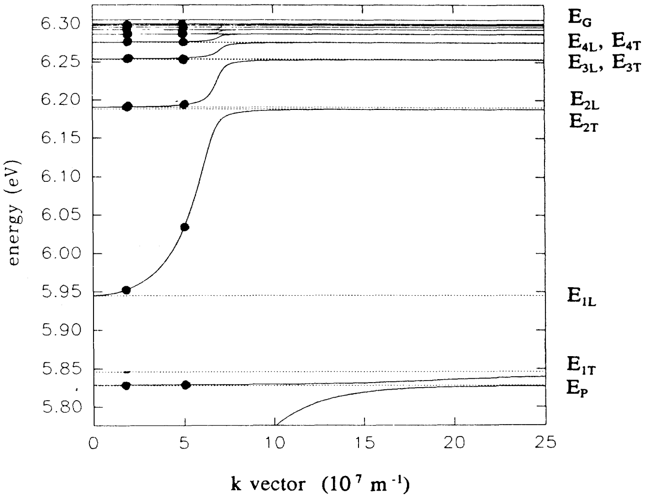

FIG. 1. Polariton diagram with $n=1,2,3,\ldots$ excitons (with E_{nT} and E_{nL} representing the transverse and longitudinal excitonic energies) and the triplet $F=2$ paraexciton with energy E_P.

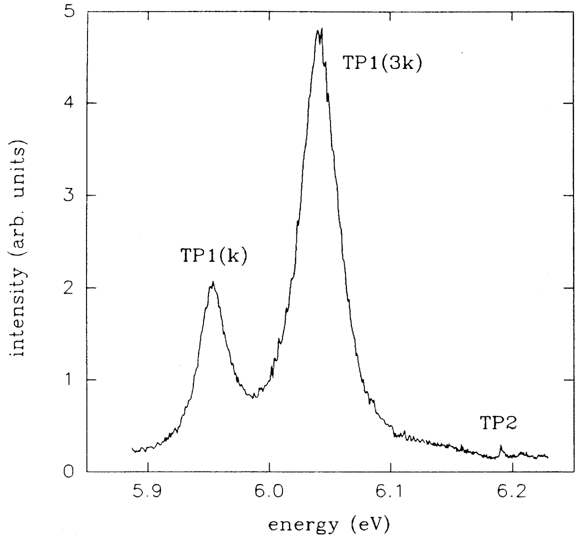

FIG. 2. Typical excitation spectrum of KI at 9 K and 0 bar, covering the $n=1$ (denoted as TP1) *and* $n=2$ (denoted as TP2) polariton regions.

TP($3k$)—whereas the TP(k) are generated when one of the three polaritons is reflected at the backside of the crystal or the cell window, thus creating a polariton still having total energy E, but now total wave vector $k \approx 1.7\times 10^7\ \mathrm{m}^{-1}$ ($=2k-k$).

In Ref. 5, we observed the pressure-induced blueshift of the $n=1$ transverse and $n=1$ longitudinal energies and a decrease in the curvature at $k=0$ of the transverse polariton branch lying between E_{1L} and E_{2T}. It was also found that the linewidth of the excitation maxima decreased significantly with increasing pressure. This work has been extended to include observations of the $n=2$ exciton polariton and the nominally forbidden $F=2$ paraexciton under pressure. Figure 2 displays a typical excitation spectrum of the $n=1$ polariton [$\mathrm{TP}_1(k)$ and $\mathrm{TP}_1(3k)$] and $n=2$ polariton TP_2 covering the energy range from about 5.9 to 6.25 eV. Knowing the energies E_{nT} of the $n=1$ and $n=2$ exciton and their pressure dependence, we could calculate values for the excitonic binding energy and the energy gap together with their pressure dependences within the validity of the approximation such that the usual hydrogenic series $E_{nT}=E_G-E_B/n^2$ holds. (This approximation will be discussed in some detail later in the paper.) Measuring the $F=2$ paraexciton and its pressure dependence enabled us to find the pressure dependence of the electron-hole exchange energy as defined by Onodera and Toyozawa.[6]

II. EXPERIMENTAL ASPECTS

The experimental setup has been previously described in more detail.[5] We only want to mention that, for the experiments described here, the intensities used for the incoming light had to be substantially higher than those used studying the $n=1$ exciton-polariton structure. Most measurements were done with an estimated intensity ranging from 0.5 to 1 GW/cm^2 in the sample with typical pulse energies of 10 μJ or more. At intensities higher than 1 GW/cm^2, the crystal would show signs of damage, but nothing was found to indicate a dependence of the measured energies on pump intensity. Successful population of the polariton states in question was observed by monitoring the luminescence emanating from the self-trapped exciton. The temperature range throughout this work was between 9 and 10 K. The energy of the $n=1$ (exciton)-polariton level is substantially independent of temperature below 15 K, whereas the $n=2$ level starts decreasing at about 10 K. The same can be said for the increase of the half-width. A thorough investigation of the pressure and temperature dependence of the (exciton)-polariton states of KI and RbI will be published elsewhere. The pressure range extended up to 3 kbar, which is sufficient to generate accurate measure of the linear pressure dependencies. The uncertainty in the pressure measurements is estimated to be about ±10 bar.

III. RESULTS AND DISCUSSION

Figures 3(a) and 3(b) show the excitation spectrum of the $n=2$ polariton at two different pressures at about 10 K. The three maxima are identified as the zero-phonon $2s$ exciton polariton with no phonon involved in its creation, and the one- and two-phonon sidebands. The negative slope at energies lower than the first maximum is caused by the wing of the $\mathrm{TP}_1(3k)$ excitation of the $n=1$ polariton.

It can be seen in Fig. 2 that the $n=2$ exciton polariton is much smaller in intensity than the corresponding $n=1$ structure. In one-photon experiments, the value for the oscillator strength f_1 of the $n=1$ exciton polariton has been determined to be 0.36 (Ref. 7) and 0.33.[8] In Ref. 8, the ratio of the oscillator strengths f_2/f_1 is calculated to be 0.17, which is close to the theoretically expected

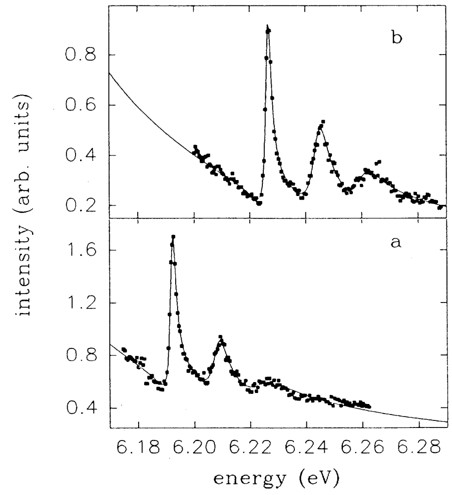

FIG. 3. (a) The $n=2$ polariton excitation spectrum of KI at 85 bar and 9.0 K. The solid line represents the nonlinear least-squares best fit. (b) The same at 2585 bar and 9.0 K.

value[9] of $\frac{1}{8}$ because of the proportionality of the oscillator strength to $1/n^3$. In our case the peak ratio is more like $\frac{1}{50}$.

Beyond these sidebands, we observed no additional structure before the band gap. In particular, there were no signs of the 3s exciton. The 3s exciton would be expected to be lower in intensity by at least a factor $\frac{8}{27}$, so its absence is regrettable but not surprising.

Another feature is the marked asymmetry of the excitation spectra, which is expected on the grounds of the indirect participation of other states (phonon states) in the creation process.[10] (Theoretically, this kind of coupling is expected to be stronger for the $n=2$ exciton than for the $n=1$ exciton because, for Fröhlich-type electron-hole interaction, the form factors representing effective charges of electron and hole tend to cancel each other with increasing binding energy in relation to the LO-phonon energy. This is called the cancellation effect,[11,12] and therefore the excitation spectrum for the $n=1$ polariton shows a much more symmetrical Lorentzian profile and no detectable sidebands.)

The linewidth of about 3-meV full width at half maximum (FWHM) for the zero-phonon band is much smaller than that of the $n=1$ polariton excitation [about 36-meV FWHM for the $\mathrm{TP}_1(3k)$ at zero pressure], which indicates that the $n=2$ exciton polariton has a much longer lifetime. The linewidth also seems to decrease weakly with pressure, as was observed in the case of the $n=1$ polaritons $\mathrm{TP}_1(k)$ and $\mathrm{TP}_1(3k)$, although this cannot be assured because the decrease is not as large as in the corresponding case of the $n=1$ polariton.

The zero-, one-, and two-phonon sidebands were modeled by asymmetric Lorentzians, whereas the contribution of the $n=1$ polariton structure [the $\mathrm{TP}_1(k)$ and $\mathrm{TP}_1(3k)$] was represented by the symmetric Lorentzian $\mathrm{TP}_1(3k)$ whose linewidth and peak energy were previously measured[5] and therefore kept fixed, but whose amplitude was varied in the fitting process. In the complete fitting formula [Eq. (1)], A_i represents the amplitudes, E_i the resonance energies, Γ_i the half-width ($2\Gamma_i=\mathrm{FWHM}$), and AS_i the asymmetry factors. E denotes the three-photon energy as usual.

$$I(E)=\frac{A_{3k}}{1+\left[\dfrac{E-E_{3k}}{\Gamma_{3k}}\right]^2}+\sum_{i=0}^{2}\frac{A_i\left[1+AS_i\left[\dfrac{E-E_i}{\Gamma_i}\right]\right]}{1+\left[\dfrac{E-E_i}{\Gamma_i}\right]^2}\;. \tag{1}$$

The fitting formula therefore contains 13 parameters that were varied during the fitting. Figure 4 displays the respective resonance energies versus pressure at low temperature (10 K). The linear best fits to these are (uncertainties are the threefold standard deviation as obtained from the fitting procedure)

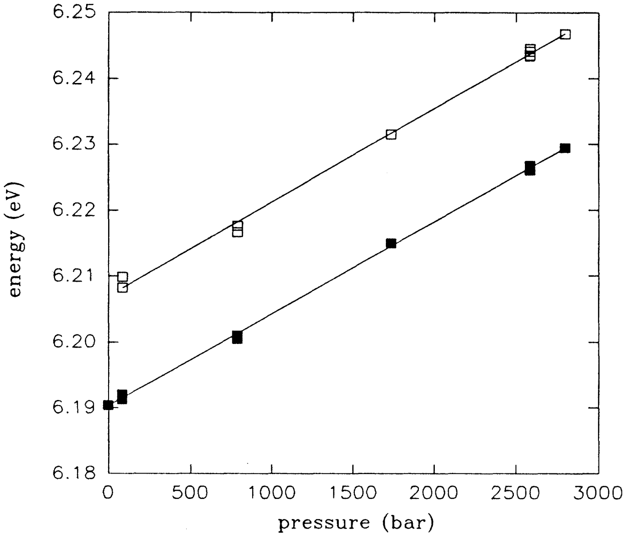

FIG. 4. Zero-phonon sideband (solid squares) and one-phonon sideband (hollow square) of the $n=2$-polariton vs pressure.

$$(6.1903\pm0.0006)\ \mathrm{eV}+(13.95\pm0.30)\ \mathrm{meV}/p\ \mathrm{kbar}\quad\text{(zero-phonon band)}\ ,$$

$$(6.2070\pm0.0015)\ \mathrm{eV}+(14.2\pm0.8)\ \mathrm{meV}/p\ \mathrm{kbar}\quad\text{(one-phonon band)}\ .$$

Our value of 6.1903 eV is slightly higher than previously reported values[8,13] from one-photon experiments of 6.184 eV, but lower than the step reported in Ref. 14 (6.21 eV). The energetic difference of the zero- and one-phonon sideband of 16.7 meV corresponds to the energy of the LO phonon in KI at $q=0$ [17.6 meV (Ref. 15)], suggesting the identification of the bands as such. (The measurements reported in Ref. 15 were done at 90 K, but no significant changes are expected for 10 K.) The quality of the data near the two-phonon sideband precludes a more quantitative treatment of its pressure dependence. The pressure dependence of the energy difference between the zero- and one-phonon sidebands is not outside experimental error, but the value expected would be about

$$16.7\ \mathrm{meV}/130\times3\ \mathrm{kbar}=0.4\ \mathrm{meV/kbar}\ ,$$

where 3 represents an estimate for the Grüneisen parameter γ. [We made use here of the relation $-d\ln(E)/d\ln(V)=\gamma$ for the phonon energies.]

Previous measurements of the $n=1$ polariton together with the latest value for the longitudinal-transverse splitting of the 1s exciton[16] give the energy of the transverse exciton E_{1T}:[5]

$$(5.846\pm0.002)\ \mathrm{eV}+(16.0\pm0.4)\ \mathrm{meV}/p\ \mathrm{kbar}\ .$$

Combining these results can provide the excitonic binding energy and its pressure shift, provided that one assumes excitons with a hydrogenic energy spectrum (Wannier excitons) as long as the longitudinal-transverse splitting for the $n=2$ exciton polariton is negligible. The latter point will be discussed below. Within these assumptions, the energies of the transverse excitons at $k=0$ and their pressure shifts are

$$E_{nT}=E_g-\frac{E_B}{n^2}\ , \quad \frac{dE_{nT}}{dP}=\frac{dE_g}{dP}-\frac{1}{n^2}\frac{dE_B}{dP}\ . \tag{2}$$

From the above equations, one obtains the following experimental results:

$$E_B=(459\pm3)\ \text{meV}\ ,$$

$$dE_B/dP=(-2.7\pm0.7)\ \text{meV/kbar}\ ,$$

$$E_g=(6.305\pm0.001)\ \text{eV}\ ,$$

$$dE_g/dP=(13.3\pm0.4)\ \text{meV/kbar}\ .$$

The uncertainties are the threefold standard deviation as obtained from the fitting process.

A question remains as to the longitudinal-transverse splitting $\Delta_{2\text{LT}}$ of the 2*s* exciton. If one assumes that $\Delta_{2\text{LT}}=6.3$ meV (the difference between our measured 6.1903 eV and the 6.184 eV found in Refs. 8 and 13), one actually obtains a value of $E_B=451$ meV. The pressure shift would stay the same, however, assuming that $\Delta_{2\text{LT}}$ does not change considerably with pressure as was found to be the case for $\Delta_{1\text{LT}}$, which changed very little with pressure.[5] Also, E_G would drop to 6.297 eV, but the pressure shift of the band gap would stay the same.

The above results imply that the excitonic binding energy decreases with pressure, a result in contrast to recent measurements of excitons in GaAs, where the excitonic binding energy increased substantially.[17] The excitonic binding energy can be expressed as

$$E_B=\frac{\mu\left[\dfrac{e^2}{4\pi\varepsilon_{\text{vac}}}\right]^2}{2\hbar^2\varepsilon_\infty^2}\ , \tag{3}$$

with ε_{vac} as the vacuum dielectric constant and ε_∞ as the dielectric constant [Eq. (3) is in SI units]. The use of ε_∞ for the dielectric constant is not obvious. In general, the decision of which dielectric constant to use (ε_0 or ε_∞) to describe the screening between electron and hole depends on the polaron radii of electron and hole. Fischer and Hilsch[14] have shown that the use of ε_∞ is justified for all alkali iodides, using a criterion from Haken.[18] (This enabled them to calculate the electron-hole reduced mass μ in the first place.) Since our binding energy of 459 meV is very close to theirs (450 meV), we will continue to use $0.26m_0$ as the value for the reduced mass μ. The pressure dependence of $\varepsilon_\infty=n^2$ has been measured.[19] From those pressure data one finds that, for pressures lower than 3 kbar,

$$\varepsilon_\infty=n^2=2.82+0.013\ \text{kbar}^{-1}p\ .$$

From Eq. (3), one can derive

$$\frac{1}{E_B}\frac{dE_B}{dP}=\frac{1}{\mu}\frac{d\mu}{dP}-\frac{2}{\varepsilon_\infty}\frac{d\varepsilon_\infty}{dP}\ , \tag{4}$$

and from this relationship one can calculate the change of the reduced mass μ with pressure. The result is

$$d\mu/dP=+8.7\times10^{-4}m_0/\text{kbar}\ .$$

The Bohr radius of the exciton can be expressed as

$$a_B=a_0\frac{\varepsilon_\infty}{\mu/m_0}\ , \tag{5}$$

with a_0 the Bohr radius of the hydrogen atom of 0.529 Å. This equation can be used to find the pressure shift of the Bohr radius of the exciton in the same way as Eq. (4) was used to find the pressure shift of the reduced mass once the behavior of ε_∞ was determined:

$$\frac{1}{a_B}\frac{da_B}{dP}=\frac{1}{\varepsilon_\infty}\frac{d\varepsilon_\infty}{dP}-\frac{1}{\mu}\frac{d\mu}{dP}\ . \tag{6}$$

Therefore, with the values of E_B, μ, and their pressure shifts one finds that the fractional change $(1/a_B\, da_B/dP)$ in a_B is + 0.13% per kbar, which has to be compared to about a -0.25% change per kbar in the lattice constant of KI. The value for the excitonic Bohr radius using Eq. (5) itself is 5.74 Å, and for the pressure shift one obtains

$$da_B/dP=+7.2\times10^{-3}\ \text{Å/kbar}\ .$$

A note has to be added about the validity of the hydrogenic model for excitons in KI. This question has to be addressed because the hydrogenic model often is only valid for excitons with a quantum number n higher than 1. Since I^- is isoelectronic with Xe, one can ask how well the hydrogenic model works there. The parameter describing the inadequacy of the hydrogenic model is the "hydrogenic defect,"[20] which gives the central cell correction by which the binding energy of the first exciton E_B^1 differs from the binding energy E_B one would expect to find by looking at the $n=2,3,\ldots$ members of the hydrogenic series. For Xe this means a 7% change (the measured $n=1$ exciton energy is lower than the one calculated using the energy values of the $n=2$ and $n=3$ excitons).[21] For KI, a smaller value is expected since the wave function of the first exciton stretches out to beyond nearest-neighbor distance,[22] whereas for Xe it is basically the atomic radius itself.[23] Unfortunately, the $n=3$ exciton which would have provided the data for an evaluation of the hydrogenic defect could not be observed (and it is not expected to be observed, as can be determined by looking at the decrease of the strength of the transition going from the $n=1$ to the $n=2$ exciton). However, the $n=3$ exciton has recently been observed in CsI, and the hydrogenic defect has been found to be insignificant in this case.[24] On the other hand, there is one publication known to us that claims to have observed the $n=3$ exciton in KI (Ref. 25) by identifying *minima* in one-photon excitation spectra of the total luminescence of KI based on the observation that those *minima* would coincide with *maxima* observed in one-photon absorption spectra. Values found there are $\mu=0.21m_0$ and $E_B=0.36$ eV, calculated from the positions of the $n=2$ and 3 excitonic *minima*. The observed $n=1$ excitonic *minimum* there is 0.1 eV lower than the calculated position of 5.95 eV based on the $n=2$ and 3 exciton states. E_g is 6.31 eV.[25] This may limit the validity of our calculations of the binding energy and band gap.

$F=2$ paraexciton versus pressure, exchange energy

Onodera and Toyozawa evaluated the exchange interaction between the electron and hole by separating it into an analytic and nonanalytic component.[6] Since the value of the spin-orbit-splitting parameter λ (about 1 eV) is so much bigger than the exchange energy (the analytic part) in the case of alkali iodides, an approximation can be made that gives this exchange energy Δ_{ex} as

$$\Delta_{ex}=\tfrac{3}{2}(E_{1T}-E_P) , \tag{7}$$

where E_{1T} denotes the energy of the first transverse exciton and E_P the energy of the $F=2$ paraexciton.

Earlier one-photon experiments[26,27] showed small structures that were interpreted as phonon-assisted transitions involving the triplet state. Those experiments found values of 43 meV (Ref. 26) and 40 meV (Ref. 27) for the exchange energy (as defined by Onodera and Toyozawa).[6] One-photon experiments have particular difficulties measuring the true position because of the high k-vector values inherent in one-photon experiments on very strongly absorbing systems. The one-photon data require the inclusion of the mixing of light and heavy excitons into the theory.[28,29]

Beerwerth and Fröhlich were the first to directly measure the $F=2$ paraexciton using the method of three-photon spectroscopy introduced by them.[29] They used intense magnetic fields so that the disallowed transition would gain oscillator strength through the admixture of the $F=1$ exciton states. However, the transition should also gain oscillator strength for k vectors different from zero, as already stated in the Introduction. Beerwerth and Fröhlich measured (5.8279 ± 0.0001) eV as the energy of the paraexciton, 0.25 meV for the half-width, and even found the splitting between the Γ_5^- and Γ_3^- substates to be 0.1 meV. The most recent value for the exchange energy Δ_{ex} given by Fröhlich *et al.* is 29 meV (Ref. 16) (using the definition of Onodera and Toyozawa).

Recently a one-photon experiment also succeeded in measuring the position of the paraexciton directly[4] by measuring luminescence and absorption spectra of KI samples of thicknesses between 0.1 and 10 μm and extrapolating these values to bulk crystals. In those experiments the paraexciton was observed to have an energy of 5.831 eV and Δ_{ex} was found to be 20 meV.

We succeeded in measuring the $F=2$ paraexciton for several pressures, probably the first observation of that pressure dependence. The overall signal intensity was very weak; Ref. 29 reports about one detected photon for 10^{16} incoming photons. Figure 5 shows the three-photon excitation spectrum at 502 bar and 9.7 K. The incoming radiation was circularly polarized to suppress the overpowering influence of the $F=1$ exciton polariton as described by Beerwerth and Fröhlich[30] and recommended on a theoretical basis by Pasquarello and Andreani.[31] Indeed, none of the scans done with linear polarization succeeded in detecting the transition. Figure 6 shows the peak-energy position versus pressure. Without taking the zero-pressure data point of Ref. 29 into account, we obtain, for the behavior of the paraexciton under pressure,

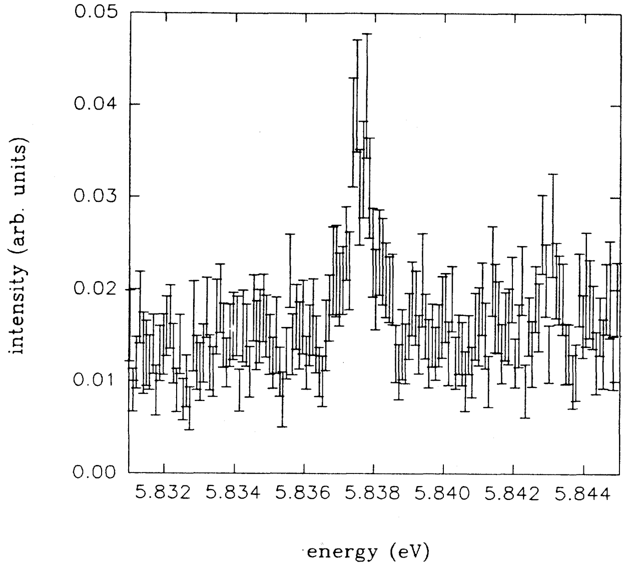

FIG. 5. The $F=2$ pareaexciton excitation spectrum at 502 bar and 9.7 K. The error bars represent the single standard deviation.

$$E_p=(5.829\pm0.002)\ \text{eV}+(16.5\pm0.3)\ \text{meV}/p\ \text{kbar} .$$

The uncertainties are the threefold of the standard deviation. Including the zero-pressure value,[29] we have 5.828 eV for E_P and 17.1 meV/kbar for the pressure shift with the same uncertainties.

Recalling the corresponding values for the first transverse exciton (5.846 eV for the offset and 16.0 meV/kbar for the shift), the exchange energy is

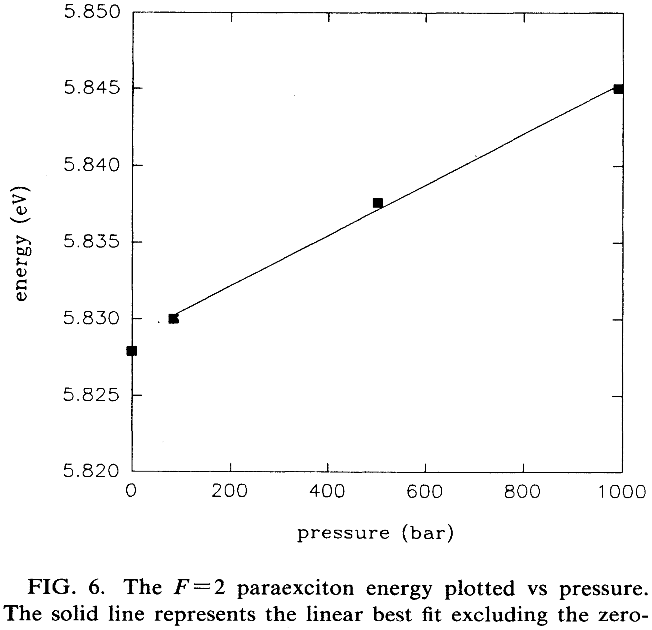

FIG. 6. The $F=2$ paraexciton energy plotted vs pressure. The solid line represents the linear best fit excluding the zero-bar pressure point from Ref. 29.

$$\Delta_{ex}=(26\pm3)\ \text{meV}-(0.8\pm0.8)\ \text{meV/kbar}\ .$$

The corresponding values including the zero-pressure point would be (27 ± 3) meV for the exchange energy and $-(1.7\pm0.8)$ meV/kbar for its pressure shift. The data seem to indicate that a slight reduction in the exchange energy occurs with compression, but barely if at all outside the threefold standard deviation.

Very recently Fröhlich *et al.* reported that they have measured the paraexciton in KI under uniaxial stress for different directions in the crystal ([001], [110], and [111]) and found the values for the hydrostatic, tetragonal, and trigonal deformation potentials,[32] although they have not yet been published.

IV. CONCLUSION

We have measured the $n=2$ exciton-polariton structure of KI under hydrostatic pressure using three-photon spectroscopy. Together with previously published data of the $n=1$ exciton polariton, we were able to derive values for the excitonic binding energy and its pressure shift as well as for the band gap and its behavior under pressure. Our calculation is based on the assumption that the longitudinal-transverse splitting of the $n=2$ exciton polariton and the hydrogenic defect for the $n=1$ exciton energy are negligible. We also succeeded in measuring the hydrostatic pressure dependence of the $F=2$ paraexciton and thus the (transverse) exchange energy of electron and hole for pressures smaller than 1 kbar. Both our results demonstrate the importance of this technique. First, it would have been quite difficult if not impossible to measure the $n=2$ state under pressure using one-photon spectroscopy of bulk KI. Second, the paraexciton would have been one photon forbidden and also undetectable in bulk material.

ACKNOWLEDGMENT

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