suggesting different vertical distances from the immediately underlying atomic plane. This is not consistent with either of the lateral-displacement reconstruction models thus far proposed,[1,2] but is consistent with and supports the vertical-displacement model of FBE,[3] with the possible inclusion of some new features. In addition to the vertical displacement periodicity of atoms along the ⟨010⟩ directions, there may be some other displacement periodicities, so that there are at least three classes of displacements, accounting for our observation of the $p(2\times2)$ structure. Also, we cannot exclude the possibility that the atoms are displaced laterally, to some extent,[10] as well as vertically. In any case, the evidence implies a periodic variation of effective binding energies. We find no inhibiting effects because of the proximity of single-atom-height plane edges.

We wish to emphasize that our evidence for a $c(2\times2)$ structure of {001}W extends from ~15 to 460 K, the lower and upper limits of which range extend beyond the range reported in related work by other techniques. The fact that we find clear evidence for reconstruction at the higher temperatures may mean that the reconstructed configuration prevails over most of the temperature range of existence of stable clean {001}W planes (e.g., at least from ~15 K up to temperatures when surface diffusion becomes prevalent). If this is so, then the configuration does not result from any structural phase transition, but rather represents the true {001}W atomic structure. Alternatively, the persistence of reconstruction at the higher temperatures may be due to the influence of the strong electric field of the FIM.

A more detailed exposition will be given in the near future.

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Excited-State Absorption Spectrum of F_2^+ Centers and the H_2^+ Molecular-Ion Model

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Five principal transitions, three of which from the first excited state, have been measured in absorption for the F_2^+ center in KF. With one significant exception, these data are in essential agreement with predictions of the simple H_2^+ molecular-ion model. The measurements were made by way of a novel optical pumping technique, which allows for direct, accurate determination of band strengths and shapes, even in the presence of strong overlapping absorptions by other species.

As a single electron trapped by a pair of adjacent anion vacancies, the F_2^+ center has been compared to an H_2^+ molecular ion embedded in a dielectric continuum.[1] That model was given considerable support by measurements in KCl, principally on the $1s\sigma_g \rightarrow 2p\sigma_u$ (Refs. 2 and 3) and $1s\sigma_g \rightarrow 2p\pi_u$ (Ref. 3) transitions (see Fig. 1). Furthermore, the model has been quite useful in predicting and interpreting phenomena relating to F_2^+ center lasers.[4-6] Nevertheless, the predictive abilities of such a model are limited, and a rather complete empirical determination of the electronic structure is ultimately required. This Letter describes such a determination, involving measurement in KF of all *five* of the principal transitions indicated in Fig. 1. Based on modu-

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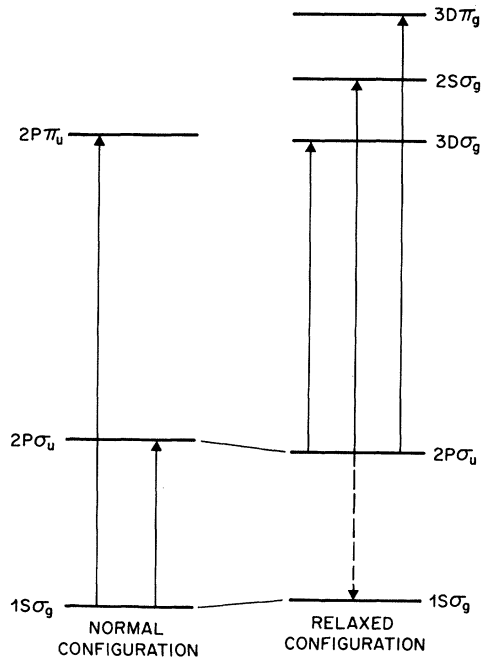

FIG. 1. Energy levels of the F_2^+ center in KF as determined by the measurements reported in this Letter. All five of the transitions indicated by solid vertical lines have been seen in direct absorption. The dashed vertical line indicates emission. (See text.)

lated pumping of the $1s\sigma_g \rightarrow 2p\sigma_u$ transition in fully oriented samples, the measurements were essentially via direct absorption. (In previous work,[3] only transitions originating from the ground state were seen, and all but one of those were measured by fluorescence excitation.) Thus, in addition to the extra transition energies revealed, the measurements described here allow for direct and precise intercomparison of all oscillator strengths, and for accurate determination of band shapes and polarizations. Remarkably, the new measurements largely conform to the model, at least on a coarse scale. However, it is not surprising that they also reveal some significant deviations, particularly in the precise energies and ordering of the higher excited states.

Figure 2 is a schematic of the apparatus. The samples ([100] slabs of KF, ~1 mm thick, mounted on a 77°K cold finger) were oriented such that a [110] axis lay in the plane of the figure; essentially all the F_2^+ centers were aligned along that particular axis. The pump beam [~5 W at 1.064 μm from a Nd:YAlG (neodymium-doped yttrium-aluminum-garnet) laser] was symmetrically modulated ($f_m = 50$ kHz) between $E_\parallel$ (in the plane of the figure and parallel to the [110] axis) and $E_\perp$ polarizations. A tunable monitor beam of fixed polarization (either $E_\parallel$ or $E_\perp$) was carefully focused on to the same 0.5-mm-diam spot as the pump beam. The modulated pumping (acting on the fundamental transition of fully oriented centers) created time-dependent populations of equal amplitude in the $2p\sigma_u$ state (in phase with the pump) and in the $1s\sigma_g$ state (180° out of phase with the pump). Thus absorption transitions originating from the $2p\sigma_u$ state yielded signals *out of phase* with the pump, while absorptions originat-

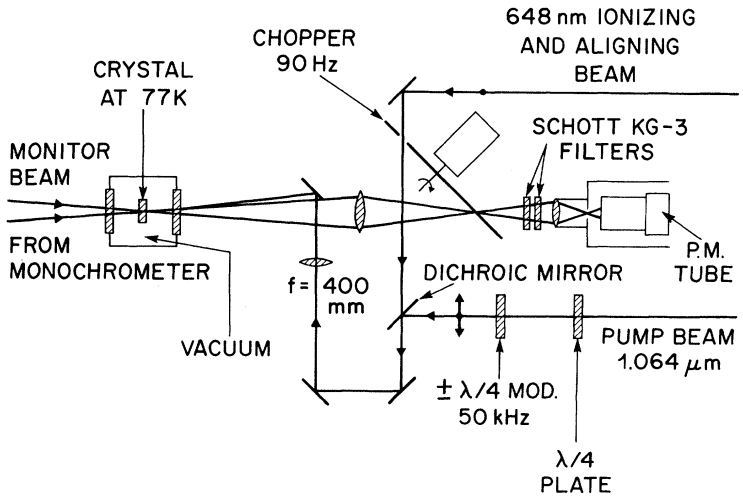

FIG. 2. Schematic of the apparatus. The Schott KG-3 filters rejected scattered pump light at 1.064 μm; for measurement in the neighborhood of the fundamental transition, these were replaced by a dual-grating spectrometer. For other details, see text.

ing from the ground state appeared *in phase*.

An electronic feedback system[7] kept the time-average photomultiplier output current precisely fixed ($I_{dc}=1$ μA), such that the 50-kHz lockin signals would accurately represent the absorption band strengths and shapes. Also, in this way the measurements were unaffected by interfering absorptions from other species: In the first place, since only the F_2^+-center populations were modulated, only they yielded signals. Second, the electronic normalization made it possible to "look through" interfering absorptions, with no distortion in either shape or strength of the desired band, just as long as enough monitor light leaked through the sample to allow for good signal-to-noise ratio.[8] Thus, the manifold and somewhat dubious corrections required by the selective excitation technique[3] were completely obviated.

The second laser beam (~3 W at 648 nm, $E_\perp$ from a Kr^+-ion laser) served two functions at once: First, by acting on the F_2 band, it continuously reionized the centers through a two-step process that has been described elsewhere.[9] Second, by promoting the second step of the process $1s\sigma_g \rightarrow 2p\sigma_u \rightarrow 3d\sigma_g$, it allowed for continual reorientation of the centers back to the desired [110] axis, also as described elsewhere.[6] A chopping wheel ($f=90$ Hz) alternately blocked the detector and the second laser beam, such that stray light from the latter would not affect the signals. The sample rejuvenation thus afforded by the second laser was vital in combating degenerative effects, especially those of the monitor beam itself in the near uv.

The signals are shown in Fig. 3; also tabulated there are the relative oscillator strengths, as determined from the areas under the bands, and theoretical values from the model.[10] For discussion of fully oriented centers, it is appropriate to define an "effective oscillator strength," $f_0(\hat{e}) \equiv 2E_{ba}|\langle b|\hat{\mathbf{r}}\cdot\hat{e}|a\rangle|^2$ for the transition $a\rightarrow b$ (all quantities are in atomic units). That is, f_0 is just the usual oscillator strength for light of polarization direction $\hat{e}$, but without the factor $\frac{1}{3}g$, where g is the degeneracy factor. The integrated band strengths in Fig. 3 should be directly proportional to the f_0 values. In view of the rather high sensitivity of oscillator strengths to distortion of the wave functions, the correspondences indicated in Fig. 3 are truly remarkable. Also, the polarizations are essentially perfect: For $e \lesssim 2.7$ eV, the $E_\perp$ signals were less than 1% of the $E_\parallel$ signals, and a similar comment applies to the $E_\parallel$ signals for $E \gtrsim 2.7$ eV.

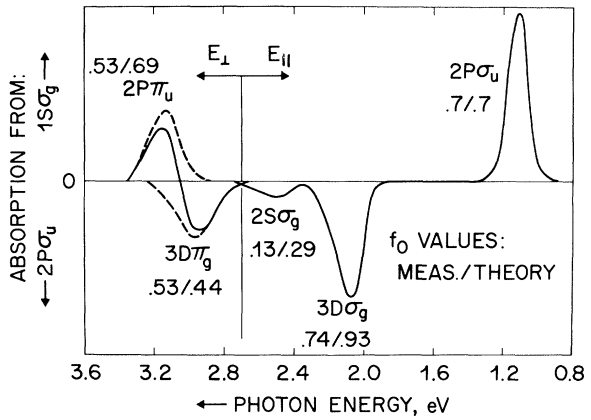

FIG. 3. Absorption signals generated by the modulated pumping technique. $E_\parallel$ and $E_\perp$ refer to polarization of the monitor beam. Partial overlap of the two highest-energy transitions results in some degree of cancellation; reconstructed bands are shown in dashed outline. Because of strong luminescence, the long-wavelength tail of the fundamental absorption could not be measured with this technique, but it was easily reconstructed from standard absorption measurements. The measured f_0 values are based on areas under the curves, with f_0 of the fundamental somewhat arbitrarily set equal to the theoretical value. For other details, see text.

According to the model, energy levels are to be calculated from $E_{F_2^+} = k_0^{-2} E_{H_2^+}(r_{12})$, where the proton separation r_{12} is given by $k_0^{-1}R_{12}$; here k_0 is the dielectric constant and R_{12} the actual vacancy-pair separation.[11] By making slight adjustments in r_{12} and k_0, one can obtain an exact fit of the calculated to experimental values for the first two ground- to exicted-state transition energies. In KF, the "best-fit" parameters obtained in this way are $r_{12}=3.25$ a.u. and $k_0=2.084$. Furthermore, by allowing r_{12} to relax to 3.55 a.u., one can account for the observed Stokes shift (between absorption and emission) of the fundamental transition. Thus far, the fitting process is like that described in Ref. 3. It does not constitute a very severe test, since only two quantities are fitted with two independent adjustable parameters.

However, here we have three more positively identified transitions with well-defined energies to compare with the model, but where no further adjustment of the parameters is possible. The $2p\sigma_u \rightarrow 3d\pi_g$ and $2p\sigma_u \rightarrow 2s\sigma_g$ energies (2.94 and 2.50 eV, respectively) calculated on the basis of the best-fit k_0 and the relaxed r_{12} given above almost perfectly match the measured values.[12] (See Fig. 3.) Unfortunately, the calculated value

of 2.69 eV for the $2p\sigma_u \rightarrow 3d\sigma_g$ transition is ~ 29% higher than the measured value (2.08 eV). Thus, the measured level of the $3d\sigma_g$ state lies below that of $2s\sigma_g$, while the model predicts the reverse order for these two levels.[13] To be sure, in the H_2^+ molecular ion, the $2s\sigma_g$ and $3d\sigma_g$ levels do eventually cross over, but only at much larger values of r_{12} ($r_{12} \gtrsim 4.2$ a.u.). However, such a very large relaxation of r_{12} is hard to justify, and furthermore, it would seriously affect the match to the other two excited-state transitions.

It will be interesting to see if the anomalously low energy of the $3d\sigma_g$ state continues to hold in other hosts, and if a semiempirical rule can be made to describe its behavior. The corresponding experimental data should be easily attainable through use of the technique described here, since efficient laser pump sources are available to match the fundamental transition of the F_2^+ center in at least a half dozen other hosts. In the mean time, it is hoped that this Letter will stimulate the generation of an improved model.

As accurately determined here, the band shapes may also provide much useful information, especially if the measurements are repeated at liquid-He temperature.[14] The measured shapes can undoubtedly be fitted to the smoothed Poisson distributions that have been well described elsewhere.[15] The excited-state absorptions are especially interesting, with their wide and highly asymmetric shapes; these correspond to the combination of a relatively small Huang-Rhys S factor[15] and a rather large effective phonon energy. The contrast between the shapes of these excited-state absorptions and that of the fundamental transition may say much about the nature of the relaxation process.

I would like to thank J. P. Gordon and J. M. Peek for helpful discussions, and A. M. DelGaudio for considerable laboratory assistance. The crystals were grown by H. Guggenheim.

Note added—Recent measurements with use of the technique described above, but on the host NaCl, yield an absorption spectrum that is quantitatively very much like the one shown in Fig. 3; in particular, the bands appear in the same order and have approximately the same shapes. The measured band peak energies are 2.92, 2.48, 2.01, 1.76, and 1.20 eV for transitions to $2p\pi_u$, $3d\pi_g$, $2s\sigma_g$, $3d\sigma_g$, and $2p\sigma_u$, respectively. With "best-fit" parameters of $k_0 = 2.23$ and $r_{12} = 2.95$ a.u. (relaxed to 3.50 a.u.), the predicted energies are 2.92, 2.57, 2.16, 2.35, and 1.20 eV (in the same sequence). Thus, once again a reasonable fit is obtained except for the $2p\sigma_u \rightarrow 3d\sigma_g$ transition, for which the measured energy is ~ 25% lower than that predicted. Also, with the exception of the transition to $2s\sigma_g$, which is considerably stronger in NaCl than in KF, the relative band strengths in NaCl are about as shown in Fig. 3.

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[12]Although the $2p\pi_u$ and $3d\pi_g$ states are each doubly degenerate in the ionic (continuum) model, in the actual center, the degeneracies can be lifted by a component of the crystal field. In fact, when the transitions to those two states were observed in another polarization (where E is perpendicular to the particular [100] plane containing the center axis), both transitions appeared shifted by ~0.1 eV to lower energies, somewhat as seen earlier for the $1s\sigma_g \rightarrow 2p\pi_u$ transition in KCl (Ref. 3). However, because of the partial interference of the two transitions (see Fig. 3), the individual shifts, and hence the precise splittings, are not easily determined.

[13]In the assignment of transitions, distinction between $2p\sigma_u \rightarrow 2s\sigma_g$ and $2p\sigma_u \rightarrow 3d\sigma_g$ had to be made solely on the basis of relative strength. However, in view of the large ratio of strengths involved, and of the excellent match represented by the assignment given here, the alternate choice is highly improbable. Perhaps it should also be pointed out that the ratio of strengths is not a very sensitive function of r_{12}.

[14]Measurements at liquid-He temperature may be facilitated by a several-fold reduction in pump power from that cited here; the signal-to-noise ratio would still be very good. However, it should be realized that only about 10% of the incident laser power is actually

dissipated as heat in the sample, since the sample absorbs only one of two pump polarizations, and since 80% of the absorbed light is reemitted as luminescence.

[15]A rather complete description and more fundamental references to the smoothed Poisson distribution are given in J. J. Markham, in *F-Centers in Alkali Halides*, Suppl. No. 8 to *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966).