

exposure to the air during counting. It was observed that the larger readings were usually associated with higher outgassing temperatures during electron bombardment, but beyond this no consistency in the results could be found in spite of extreme care to obtain the same conditions of cleanliness and outgassing each time.

These experiments show that the chemisorption of gases on the small area available on single crystals can be studied by a tracer technique. In future measurements it appears desirable to use a method in which the surface is not exposed to the air between measurements.

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¹ Beck, Smith, and Wheeler, Proc. Roy. Soc. (London) **177A**, 62 (1941).

² O. Beck, *Advances in Catalysis*, (Academic Press, New York, 1950), Volume II, 151.

³ T. N. Rhodin, J. Am. Chem. Soc. **72**, 4343 (1950).

⁴ T. N. Rhodin, J. Am. Chem. Soc. **72**, 5691 (1950).

⁵ Calvin, Heidelberg, Reid, Tolbert, and Yankwich, *Isotopic Carbon* (John Wiley and Sons, Inc., New York, 1949).

⁶ Order of magnitude calculations involving counting efficiency and specific activity of CO₂ indicate that 1 cpm corresponds to 10¹¹ adsorbed CO₂ molecules.

The Polarized Infrared Spectrum of Potassium Bifluoride at -185°C^*

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OBSERVATIONS on the reflection spectrum of potassium bifluoride have recently been reported¹ which appear to confirm the symmetrical linear structure of the bifluoride ion in this crystal. Some time ago absorption spectra of single crystals of KHF₂ using polarized infrared radiation were obtained in this laboratory which both confirm this work and supplement it. Owing to the improved resolution of complex absorption regions which we obtained at low temperatures it seems worthwhile to present these results briefly. The spectrum is possibly unique in the wealth of combination and overtone bands which arise from a crystal of structure so simple that a detailed interpretation may be anticipated.

Consideration of intensity, isotope shift, and polarization prompts the conclusion that the infrared active fundamentals of

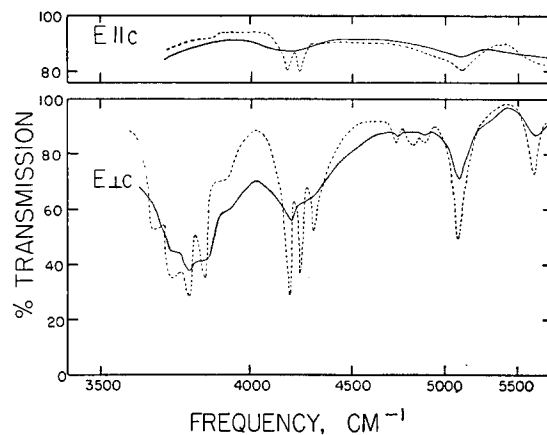


FIG. 2. Infrared spectra of KHF₂ (3300–5800 cm⁻¹) at 25°C (solid curve) and -185°C (dotted curve) in polarized light.

the bifluoride ion in KHF₂ are ν_2 (bending) $\cong 1230$ cm⁻¹ and ν_3 (antisymmetric stretch) $\cong 1425$ cm⁻¹. Raman studies² have placed the symmetric stretching frequency ν_1 at about 600 cm⁻¹. Certain features of the fundamental bands deserve comment.

The fundamentals ν_2 and ν_3 differ greatly in breadth in the absorption spectrum of thin films and in reflection.¹ The half-width ν_2 is about 30 cm⁻¹ and that of ν_3 about 200 cm⁻¹. In both KHF₂ and KDF₂ ν_3 showed no structure even at -185°C , but a narrowing of the band indicated that the breadth is at least in part due to interaction with lattice vibrations. It is surprising that such interactions are not equally manifest in the ν_2 -band. Our results confirm the splitting of the degeneracy of ν_2 previously observed in reflection, and also an apparent anomaly in the ratio of intensities observed in the two polarization aspects. One should expect $I_{||} \sim 2I_{\perp}$, but, in fact, $I_{||} \sim I_{\perp}$.³ The frequency of ν_3 is not unexpected, and is roughly that to be anticipated from the short F–F distance, but the relatively high value of ν_1 indicates a rather large positive bond-bond interaction constant in the potential function of the bifluoride ion.

As may be seen in Figs. 1 and 2 and Table I, in the range 1800–5000 cm⁻¹, the dominant absorption regions center on positions to be expected for members of the progression $\nu_3 + n\nu_1$. Structure observed in three of these regions can conceivably be due to the

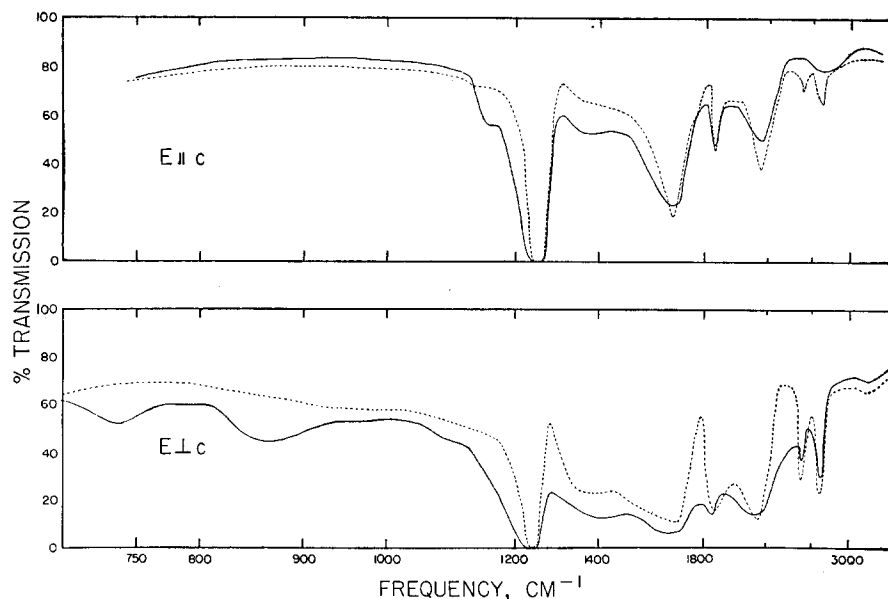


FIG. 1. Infrared spectra of KHF₂ (700–3300 cm⁻¹) at 25°C (solid curve) and -185°C (dotted curve) in polarized light.

TABLE I.

(obs) ↓	ν (cm ⁻¹) 	(calc)	<i>I</i>	Assignment
740			<i>vw</i> ^b	$\nu_2 - 490$
880		835	<i>vw</i> ^b	$\nu_3 - \nu_1$
[1170s]			<i>vw</i>	?
1230	1240		<i>vs</i>	ν_2
1425	1425	1435	<i>vs</i>	ν_3
1700	1700		<i>s</i>	$\nu_2 + 460$
1870	1870		<i>s</i>	$\nu_2 + \nu_1$
2060	2060	2065	<i>s</i>	$\nu_3 + \nu_1$
2420	2420		<i>w</i>	$\nu_2 + 2\nu_1$
2670	2670	2667	<i>ms</i>	$\nu_3 + 2\nu_1$
3240	...	3241	<i>w</i>	$\nu_3 + 3\nu_1$
3660 ^a	...		<i>vw</i>	$3\nu_2$?
3715	...		<i>w</i>	
3775	...	3787	<i>w</i>	$\nu_3 + 4\nu_1$?
3810	...		<i>w</i>	
3890	...		<i>vw</i>	$(\nu_3 + 2\nu_2)$?
4240	4240 ^a	4233	<i>w</i>	$3\nu_2$
4295 ^a	4295 ^a	4305	<i>w</i>	$\nu_3 + 5\nu_1$
4335 ^a	...		<i>vw</i>	$(\nu_3 + 2\nu_2 + \nu_1)$?
4730	...		<i>vvw</i>	$(2\nu_3 + \nu_2 + \nu_1)$?
4820 ^a	...	4795	<i>vvw</i>	$\nu_3 + 6\nu_1$
4890	...	4923	<i>vvw</i>	$3\nu_3 + \nu_1$
5085	5085		<i>w</i>	$(\nu_3 + 2\nu_2 + 2\nu_1)$?
5590	...		<i>w</i>	$(\nu_3 + 2\nu_2 + 3\nu_1)$?
(6196)				$5\nu_2$ and $(\nu_3 + 2\nu_2 + 4\nu_1)$?
(6735)				$(\nu_3 + 2\nu_2 + 5\nu_1)$?
(7326)				$(\nu_3 + 2\nu_2 + 6\nu_1)$?

Frequencies in parentheses from Ketelaar (reference 1a).

Inequality signs indicate relative intensity in two polarizations relative to tetragonal axis.

^a Observed only at -185°C . ^b Vanish at -185°C . *s* = shoulder.

near degeneracy of ν_2 and the doubling of ν_1 in the crystal. However, it is of interest that plausible assignments can be made to the individual maxima and that the overtones and combinations not involving ν_2 can be described, within the error of measurement, by a simple expression of the sort applicable to a gas spectrum. Namely, $\nu = \nu_3\omega_3 + \nu_1\omega_1 + \nu_2^2x_{33} + \nu_1^2x_{11} + \nu_1\nu_3x_{13}$, where $\omega_3 = 1447$, $\omega_1 = 614$, $x_{33} = -12$, $x_{11} = -14$, $x_{13} = 30$. The progression $\nu_2 \cong n\nu_1$ can be followed for only a short distance, but above 5000 cm^{-1} a series of moderately strong bands appear to represent the progression $\nu_3 + 2\nu_2 + n\nu_1$. The spacing of the bands seems slightly irregular, and the first two members are in doubt. At least two bands of the spectrum appear to represent combinations with a frequency of unknown origin $\sim 460\text{--}490\text{ cm}^{-1}$. This seems high for a lattice vibration but is difficult to explain otherwise. An exhaustive discussion of the spectrum must await a more satisfactory theory of overtone and combination bands in crystals than now exists.

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† Contribution No. 1597 from the Gates and Crellin Laboratories.

‡ J. A. A. Ketelaar and W. Vedder, *J. Chem. Phys.* **19**, 654 (1951).

§ See also J. A. A. Ketelaar, *Rec. trav. chim.* **60**, 523 (1941).

¶ L. Couture and J. P. Mathieu, *Compt. rend.* **230**, 1054 (1950).

* A similar phenomenon has been observed before and is as yet unexplained. See R. Newman and R. S. Halford, *J. Chem. Phys.* **18**, 1276 (1950).

High Resolution Mass Spectrometry

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IN a recent note in this Journal, Kniebes *et al.*¹ showed mass spectra of ion pairs having similar m/e which were obtained on a commercial mass spectrometer.² The present note briefly discusses some factors involved in obtaining high resolution, presents some improved results, and explains the difficulty which Kniebes *et al.* had in separating certain pairs.

The inherent resolving power of a mass spectrometer depends upon two factors: (a) the width of the ion beam at the focal plane, and (b) the mass dispersion of the instrument. The shape of peaks in a recorded spectrum depends upon these two factors

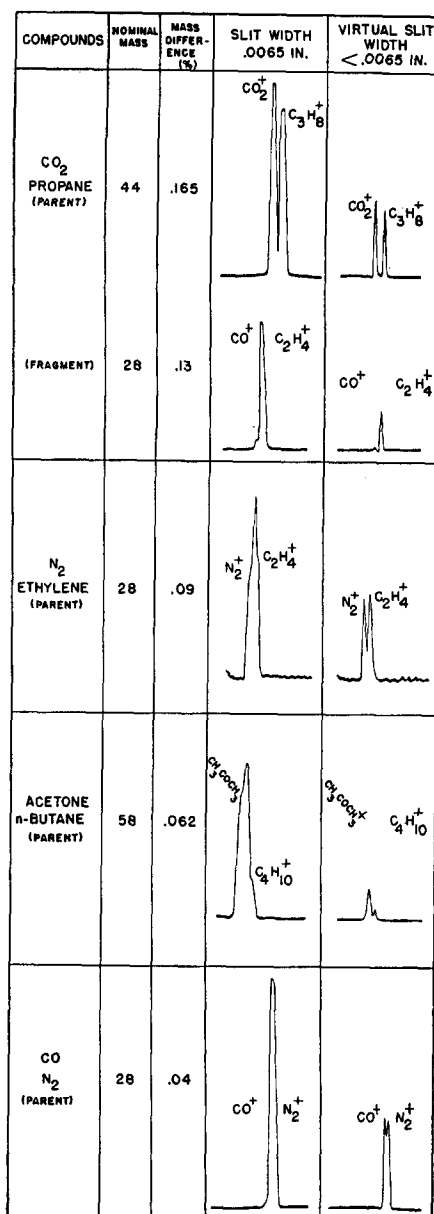


FIG. 1. Resolution of ion pairs. Resolution obtained on 180° analytical mass spectrometer, using narrow resolving slit (0.0065 in.). Improvement obtained by use of ion-optical means of reducing slit to virtual width less than 0.0065 in. is shown in column at right.

and also upon their relation to the width of the resolving slit. In general, two adjacent ion beams will show a clean separation when their dispersion is \geq the width of either beam plus the width of the resolving slit.

In analytical mass spectrometers it is necessary that the resolving slit be wider than the ion beam in order that the recorded peak height will be an accurate measure of the intensity of the beam. However, for certain qualitative or rough quantitative applications it is possible to use a resolving-slit width \leq the width of the ion beam. In the 180° , five-inch radius instruments used in reference 1 and for the work reported here, the apparent width of the resolving slit can be varied by an ion-optical method, the details of which will be published subsequently. We refer to the slit produced by this method as the *virtual* resolving slit, to distinguish it from the actual mechanical resolving slit.

The conditions under which we were able to attain improved