Dissociation Energy of Fluorine

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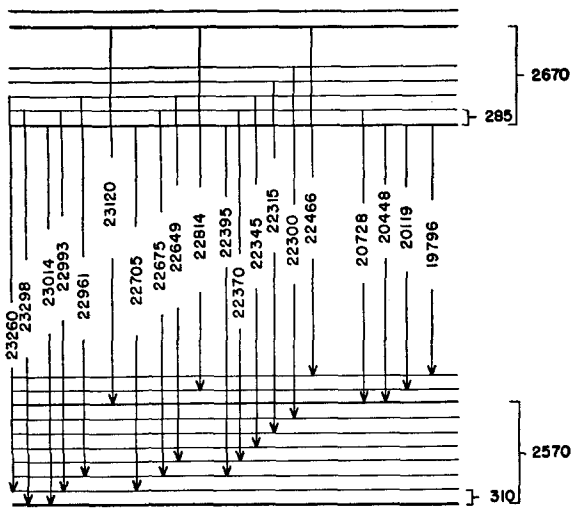

FIG. 2. Term diagram showing relative energy levels of the emitter of the blue bands; units in cm^{-1}.

bands are produced in emission under conditions where an excess of boron is present. It is possible that the large observed value of $\Delta\nu(\sim 2600\ cm^{-1})$ is associated with a B—O stretching motion.

The authors wish to thank Professor A. W. Laubengayer for providing them with samples of boron used in this work.

[1] Boron produced by this method is generally referred to as Moissan boron. [H. Moissan, Ann. Chem. Phys. (7), 6, 296 (1895)]. The "purified" product contains a few percent Mg which is chemically combined with boron.
[2] Soulen, Sthapitanonda, and Margrave, J. Phys. Chem. 59, 132 (1955).
[3] Porter, Inghram and Chupka, J. Chem. Phys. (to be published).

Dissociation Energy of Fluorine*

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IT is possible to determine the dissociation energy of a gas in which a shock wave is propagating if two parameters of the shock wave can be measured. However, the propagation velocity is the only parameter which can be measured conveniently with precision. If the shock wave were produced in a shock tube and the diaphragm bursting were ideal, a knowledge of the initial pressure ratio across the diaphragm and a velocity measurement would suffice.[1] Unfortunately, energy is always dissipated during the breaking process and the shock strength is less than that calculated under ideal conditions.[2] It occurred to us that this difficulty could be circumvented by studying the variation of velocity with composition in a gas mixture. In that case the high and low pressures can be kept constant so that if the dissipation does not change, the slope of the velocity *vs* composition curve is sufficient to determine the dissociation energy.

Measurements were carried out in a monel shock tube approximately 2 inches in diameter. The high pressure gas was He at 750 psi (3880 cm Hg) and the low pressure gas a mixture of F_2 and A, varying from 0 to 20% (by weight) F_2, at a pressure of 1 cm Hg. The velocity was measured by means of electrode probes at 50 cm intervals across which a potential near breakdown was applied. When the shock front passed, the change in discharge current was recorded as a pip on an oscillograph.

The velocities measured in the first interval, beginning at 100 cm from the diaphragm, are shown in Fig. 1. For comparison, theoretical curves are included for ideal diaphragm bursting and three different values of the dissociation energy, assuming complete dissociation ($\alpha=1$). The value of 35.8 kcal is that found by Doescher from high-temperature pressure measurements.[3]

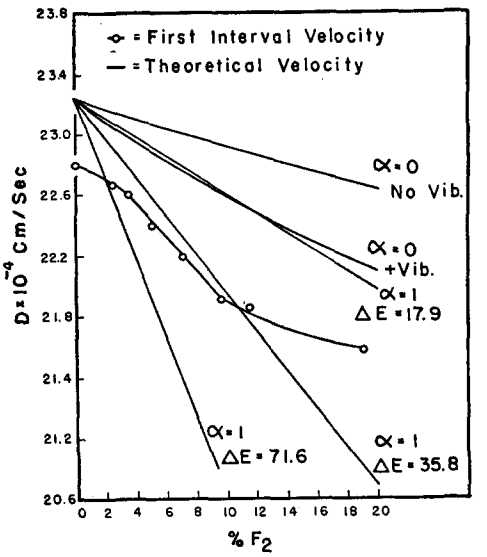

FIG. 1. Shock wave velocity as a function of fluorine composition. Both the experimental curve and theoretical curves are shown. All curves are based on a helium driver pressure of 750 psi and an expansion chamber pressure of 1 cm Hg.

Curves are also included for no dissociation ($\alpha=0$), with and without vibrational equilibration. The theoretical temperatures in the shock waves under these same conditions are shown in Fig. 2.

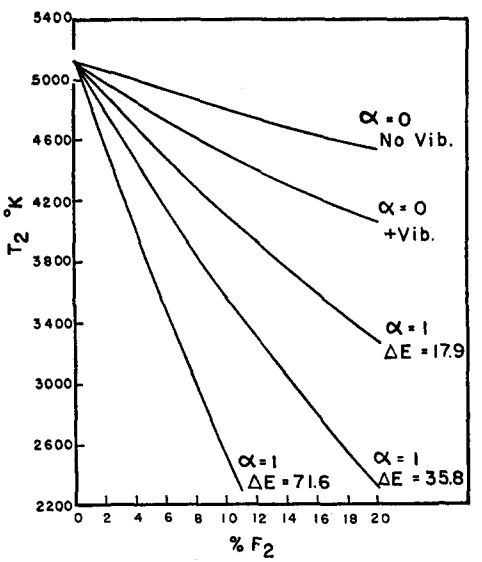

FIG. 2. Theoretical temperature behind the shock front as a function of fluorine composition.

It is seen from Fig. 1 that at compositions between 2.5% and 9.7% F_2, the velocities fall on an approximately straight line whose slope (along with the slopes from the other velocity intervals) yields $\Delta E=31.0\pm4.3$ kcal/mole, the probable error being evaluated from the scatter in the experimental velocities. An independent upper limit to the dissociation energy can also be obtained from the absolute value of the velocity, assuming the gas to be in equilibrium. At 9.0% F_2 the velocity yields an upper limit $\Delta E<38.4$ kcal/mole.

These results are satisfying but both below 2.5% F_2 and above 9.7% F_2 the results deviate from the expected behavior. The

"low" values obtained near the pure argon limit may well arise from the dissociation of impurities or other phenomena connected with the very high temperatures (Fig. 2). On the other hand, the deviation at higher fluorine concentrations may be connected with the failure to reach equilibrium at the lower temperatures. These problems are still under investigation.

Nevertheless, on the basis of this data it seems likely that the correct value for ΔE is about 31 kcal/mole and that the electron impact data recently reported must be explained by means other than a high value for ΔE.[4]

* Work supported by the Office of Naval Research.
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[1] G. T. Reynolds, "A preliminary study of plane shock waves formed by bursting diaphragms in a tube," OSRD Report No. 1519 (June, 1943).
[2] Bleakney, Wiemer, and Fletcher, Rev. Sci. Instr. **20**, 807 (1949).
[3] R. N. Doescher, J. Chem. Phys. **20**, 330 (1952).
[4] J. L. Margrave, J. Chem. Phys. **24**, 476 (1956).

Near Ultraviolet Absorption Spectrum of Tropolone Vapor

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THE absorption spectrum of tropolone vapor in 3375–3915 A region was photographed with a quartz spectrograph (13 A/mm) and a 3-m focus concave grating spectrograph in the second order (2.6 A/mm). The absorption path length was 40 cm in the vapor over the substance[1] at temperatures between 40 and 145°C. The strongest band is a doublet at 3699.53 A, consisting of sharp components with 3.5 cm^{-1} separation (reproduced in Fig. 1), of which the stronger and shorter-wave one was assumed

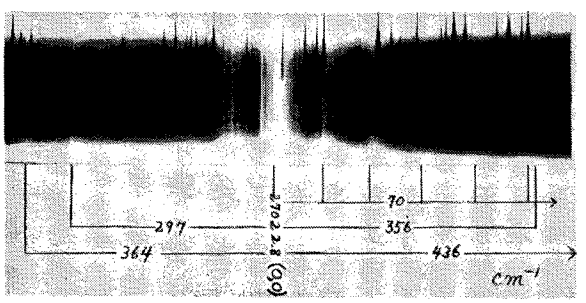

FIG. 1.

to be the 0,0 transition. On the violet side of this band, about 220 bands were observed at 40~50°C, including many very weak ones. The main progression starts from the 0,0 band with 642 cm^{-1} interval, and its four members were observed with apparent repetitions of the group pattern for the first three members.

On the red side of the 0,0 band, about 200 bands were brought out as the temperature was raised, and among them all but one of the fundamental vibrational frequencies of the tropolone molecule found in our previous Raman work[2] are identified without ambiguity, justifying the present choice of the 0,0 band.

The corresponding excited state vibrational frequencies are well represented by generally stronger bands on the violet side of the 0,0 band, which are tabulated in Table I against the ground-state frequencies. The percentage drop in these fundamental frequencies by the electronic excitation is seen to be very similar to that normally found in spectra of benzene compounds.

The 642 cm^{-1} excited state frequency (742 cm^{-1} in the ground state) which gives rise to the main progression is also found to be superposed on several other bands, so that it is highly probable that this frequency pair represents the totally symmetric breathing vibration of the seven-membered ring, analogous to the 923 (992) cm^{-1} A_{1g} benzene vibration.

TABLE I. Vibrational frequencies in tropolone (cm^{-1}).

Vapor, uv absorption		Solution, Raman effect[a]	
Ground electronic state	Excited electronic state	% drop in the excited electronic state	$\Delta\tilde{\nu}$
356	297	(83)	357 (2)
436	364	(83)	436 (1)
678	575	(85)	679 (2)
742	642	(87)	743 (3)
959	850	(89)	959 (1)
1208	1056	(87)	1208 (2)
1260	1134	(90)	1262 (4)
1417	[b]		1418 (5)
	1385		
...	1476	(92)	1610 (5)
	1552		

[a] See reference 2.
[b] Relevant band is obscured by the second member of the main progression.

The three bands shifted by 1385, 1476, and 1552 cm^{-1} from the 0,0 band on the violet side are very strong and of peculiarly diffuse nature. These frequencies may collectively represent the excited state values of the presumed C=O frequencies, to which the 1610 cm^{-1} Raman value belongs.

The sequence of several doublet bands starting from the 0,0 band on its red side having 70 cm^{-1} interval (Fig. 1) may be interpreted as v-v transitions involving the multiple excitation of the 364 (436) cm^{-1} fundamental. There remain several very strong bands in the immediate neighborhood of the 0,0 band whose origins are not clear at present.

[1] Writers are indebted to Professor T. Nôzoe of Tohoku University for the supply of tropolone sample.
[2] S. Imanishi and M. Ito, J. Chem. Soc. Japan **28**, 75 (1954).

First-Order Decomposition of Excited Aniline Molecules in the Vapor Phase*

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FROM the O_2 quenching of aniline vapor fluorescence at low pressures (1.6 mm Hg) at 70°C, Neporent[1] obtained values for the lifetime τ of the excited molecule given in Table I on the justifiable[2] assumption that the collisional quenching efficiency is unity in this case.

At 2878 A photodecomposition may be considered negligible since no fluorescence stabilization by inert gases is observed, and the reciprocal of the lifetime at this wavelength may therefore be taken as being equal to the emission constant f. At shorter wavelengths τ decreases due to an increase in the probability d of dissociation with the excess vibrational energy of the excited molecule. At the low pressures of aniline used where dissociation and emission are the only competing processes for removal of the excited molecule, d may be calculated from the relationship

$$\tau = 1/(f+d),$$

and its value at different wavelengths is given in Table I.

It has been shown in the case of β naphthylamine[3] that the vibrational heat capacity, C_{vib}, is close to the maximum value of

TABLE I. The lifetime, τ, and dissociation probability, d, of excited aniline molecules at 1.6 mm and 70°C.

	Exciting wavelength A				
	2878	2791	2670	2598	2529
$10^9\tau$ sec	7.87	6.45	4.03	3.05	1.55
$10^{-7}d$ sec^{-1}	0	1.2	10.4	19.1	50.4
T_{vib} °C		410	470	508	547