

calculations of Parr and Crawford for the two-electron problem, a value of the screening constant Z less than 3.18 formally corresponds to our result.

A crude estimate of the height of the Z' state ($\phi = \pi/2$) may be made. On the assumption of harmonic torsional potential functions for the *cis*- and *trans*-configurations of the ground state, which in the absence of interaction would cross at 95 kcal, the Z' state would lie at approximately 129 kcal (5.6 ev).

The energy required to "open the double bond" in ethylene has sometimes been deduced by methods which are erroneous in principle, e.g., as $D(C=C) - D(C-C)$ where $D(C-C)$ is for ethane, or from heats of hydrogenation, where $D(CH_2CH_2-H)$ is equated to $D(\dot{C}H_2CH_2-H)$. The above measured activation energy corresponds to this quantity for one of the two possible "opening" processes of interest in thermal reactions; namely, $C_2H_4 \rightarrow C_2H_4(N') - 61.3$ kcal. Then $D(\dot{C}H_2CH_2-H \rightarrow C_2H_4(N') + H) = 100.5$ kcal.⁷ Unfortunately, the necessary data for transformation to the perpendicular triplet state of ethylene are not available; its energy is something less than 61 kcal.

Finally, by specification of a value for $D(CH_2-H)$ (CH_2 produced in the ground state) some carbon-carbon bond dissociation energies may be indicated. $D(CH_2-H)$ has been given recently as 89.4 kcal⁸ and <87 kcal,⁹ the latter is more probably correct. We use here $D(CH_2-H) = <87$ kcal and obtain

$$\begin{aligned} D[\dot{C}H_2 - \dot{C}H_2(N')](sp^2 - sp^2) &= <60.5 \text{ kcal,} \\ D(CH_3 - \dot{C}H_2)(sp^3 - sp^2) &= <74 \text{ kcal,} \\ D(CH_3 - CH_3)(sp^3 - sp^3) &= 84.4 \text{ kcal.}^7 \end{aligned}$$

$D(CH_2=CH_2)$ is of course known independently of $L(C)$ if $D(CH_2-H)$ is known. The value used above corresponds to $D(CH_2=CH_2) = <122$ kcal.

A full report, together with some results on the rate of the reverse isomerization of pure *cis*-ethylene, d_2 will be presented later.

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The Sodium Photosensitized Isomerization of *Cis*-Butene-2*

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BUTENE-2 has a high cross section for the quenching of sodium atoms in the 3^2P state.¹ The energy given up by the excited sodium atom in the quenching collision is 48.3 kilocalories per gram atom, and the site of reception of the energy in an unsaturated molecule is probably the double bond.^{1,2} The highest energy of activation recorded for thermal *cis-trans* isomerization of ethylene derivatives is about 46 kilocalories per gram molecule.³ The fact that the energy donated to a butene molecule during the quenching collision is of the order of magnitude of the energy of activation for *cis-trans* isomerizations suggested that a study of the reactions of *cis*-butene-2 photosensitized by sodium in the 3^2P state might yield information about the distribution of energy required for isomerization.

We have investigated the sodium photosensitized reactions of *cis*-butene-2 in a quartz reaction vessel about 10 cm long and

200 cm³ in volume. The vessel, containing sodium had plane windows at both ends and was housed in a furnace fitted with windows which permitted the irradiating beam, originating in an Osira sodium lamp and filtered through a Corning filter No. 3480, to pass through the reaction vessel and out of the furnace. Weston photonic cells were used to measure roughly the intensity of the radiation, and it was estimated that the rate of absorption of radiation by the contents of the vessel under the conditions of our experiments was in excess of 2×10^{17} quanta per minute. At the pressures of butene used about 90 percent of the sodium atoms excited by absorption undergo quenching collisions with butene.¹ Consequently, the rate at which butene molecules were energized through quenching collisions was in excess of 1.8×10^{17} molecules per minute. Absorption measurements were carried out throughout the series of runs and indicated the presence of a reproducible concentration of sodium vapor in the reaction vessel at all times.

Runs of twelve hours duration were carried out with and without irradiation. The pressure of the butene was either 2 or 3 cm Hg, and the temperature of the reaction vessel (and sodium) was 170°C. The products were analyzed with a Perkin-Elmer infrared spectrometer through the cooperation of Dr. R. N. Jones of the Pure Chemistry Branch of the National Research Council of Canada. Differences in *cis*-butene-2 content of about 2 percent could be detected. The infrared absorption curves of the products were indistinguishable from the curve of the reactant (research grade *cis*-butene-2 of the Phillips Petroleum Company). It appears that isomerization was occurring to less than 2 percent, if at all. This conclusion, along with the above mentioned measurements on the absorption of radiation in the reaction vessel indicates that the quantum yield is less than 0.016. It may, of course, be much less than this.

These results show that the energy made available to the butene molecule by excited sodium atoms in the 3^2P state is inadequate to lead to *cis-trans* isomerization with high quantum yield. This may be due to the fact that the energy of activation for the "adiabatic" mechanism for isomerization⁴ is in excess of the energy given up by the sodium in a quenching collision. The results are also consistent with an energy of activation several kilocalories less than the energy yielded by the excited sodium atom if there is rapid flow of energy away from the site of reception, which is doubtlessly the double bond, since the probability of localization of sufficient energy in the appropriate torsional vibration of the double bond before collisional deactivation occurs would then be very small.

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The Flame Emission Spectrum of HBr*

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THE emission spectrum of HBr has been observed in the hydrogen-bromine flame in the fundamental region at about 2600 cm⁻¹. The gases were premixed by passing hydrogen through boiling bromine, with a hydrogen by-pass to permit moderately accurate gas ratio control. The flame was ignited by means of a spark and sustained on a 50-mesh platinum gauze of about 2 cm in diameter. Sapphire viewing windows were mounted 3 mm from the flame proper to reduce the effects of absorption by cool outer regions.

A Perkin-Elmer Model 83 monochromator with LiF optics and a PbTe detector was used in these experiments. The intensity was such that, with a Baird 450-cycle phase sensitive amplifier,

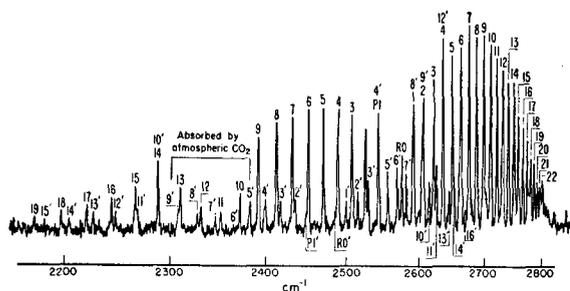


FIG. 1. The emission spectrum of HBr at approximately 1450°K.

it was possible to use an effective slit width as small as 1.6 cm^{-1} . Under these conditions, the R branch of the 1-0 band was observed out to $J=22$ with indications of a band head at $J=25$. The P branch was observed out to $J=20$. In addition, a number of lines of the 2-1 band in both P and R branches were observed. A typical spectrum is shown in Fig. 1.

Various empirical temperature determinations on a flame burning under approximately stoichiometric conditions indicate that equilibrium between the rotational and vibrational modes of excitation exists in the region of the flame *ca* 7 mm (0.02 sec) beyond the gauze. The 2-1 lines are sufficiently free from self-absorption to permit a rotational temperature to be estimated since the distribution is Boltzmann-like in character. The temperature so determined is 1430°K compared with about 1500°K for the theoretical temperature as determined by Anderson.¹ A self-absorption correction, obtained graphically from one and two path observations (using a plane mirror behind the flame to attain the second traversal), was applied to the 1-0 lines. The resultant distribution of intensities was again Boltzmann in character, and the temperature so determined was 1360°K. Using the iso-intensity method,^{2,3} the average temperature for the 1-0 band was 1390°K. All of the above temperatures are estimated to be consistent to within about 5 percent.

The vibrational temperature was estimated to be $1400^\circ\text{K} \pm 125^\circ$ using the transition probability values of Crawford and Dinsmore.⁴ As a check the rotational temperature determined from the 1-0 band of HCl, present in the flame due to a 0.3 percent chlorine impurity in the bromine, was found to be 1550°K, again to a 5 percent accuracy. No self-absorption correction was needed for this latter determination due to the low intensity of the HCl impurity spectrum.

Further work is in progress both in absorption and emission of the $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$ reaction and will be reported on in greater detail at a later date.

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A Note on the Classification of Normal Vibrations of Molecules

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IN order to indicate the essential features of normal vibrations of molecules, it is customary to classify the frequencies as stretching, deformation, rocking, wagging, etc. In fact, such a classification has been made empirically according to their wave numbers, but the rules for them are not exactly defined. At once

TABLE I. The assignment of the vibrations and the ratios of the displacements of the internal coordinates of $\text{CF}_2 = \text{CF}_2$ molecule.

ν_{obd} (cm^{-1})	Assignment	$\Delta r(\text{C}=\text{C})$	$\Delta r(\text{C}-\text{F})$	$r\Delta\beta(\text{C}-\text{C}-\text{Cl})$
ν_1 1872	C=C stretching	0.404	-0.126	-0.172
A_g ν_2 778	C-F stretching	0.052	0.099	-0.038
ν_3 394	CF_2 deformation	-0.018	-0.011	0.106
B_{1g} ν_4 1340	C-F stretching	...	-0.203	0.481
ν_5 544	CF_2 rocking	...	0.038	0.228
B_{2u} ν_6 1335	C-F stretching	...	-0.206	0.091
ν_7 245	CF_2 rocking	...	-0.002	0.131
B_{3u} ν_8 1186	C-F stretching	...	-0.159	0.140
ν_9 558	CF_2 deformation	...	0.021	0.151

it may be thought that when a certain frequency has the largest amplitude of displacement in an internal coordinate, this frequency may be called the characteristic frequency of the coordinate, irrespective of finite displacements of the others. It can, however, be easily shown that this definition does not always come up to our expectation. In Table I are shown the ratios of the amplitudes of displacements of the internal coordinates, $\Delta r(\text{C}=\text{C})$, $\Delta r(\text{C}-\text{F})$, and $r\Delta\beta(\angle\text{C}-\text{C}-\text{Cl})$ of $\text{CF}_2 = \text{CF}_2$ molecule, all of which are calculated by the use of the matrix elements L_{ik} , given in our recent article.¹ The largest amplitudes are designated by black type letters. Although the vibrations of A_g and B_{2u} groups satisfy the above definition, either of the two normal vibrations in B_{1g} group has larger amplitude in $r\Delta\beta$; therefore, according to this definition, both of them must be assigned to rocking vibration, and we have no C-F stretching vibration in this symmetry class. Further, for B_{3u} group, the vibration ν_8 , which has the frequency 1186 cm^{-1} and is obviously to be assigned to the C-F stretching frequency, has almost the same amplitude in $r\Delta\beta$ as that in $\Delta r(\text{C}-\text{F})$. Accordingly, it would be better to look for another standard for the definition of the characteristic frequencies.

Recently Torkington² and Thomas³ discussed the distribution of potential energy in the internal coordinates for each normal mode of vibration. The potential energy of the whole molecule for a given normal vibration X_k , may be expressed as

$$V = \frac{1}{2} \sum_{i,j} F_{ij} R_i R_j = \frac{1}{2} X_k^2 \sum_{i,j} L_{ik} L_{jk} F_{ij},$$

where the L_{ik} 's are the elements of the transformation matrix: $\mathbf{R} = \mathbf{L}\mathbf{X}$. If the largest term in this expression is $L_{ik}^2 F_i^2$, this frequency is to be called the R_i characteristic frequency; and particularly, if R_i corresponds to a change of a bond distance, it is called the R_i stretching frequency; and, if it corresponds to a change of a bond angle, it is called the α_i deformation or rocking

TABLE II. Potential energy terms $L_{ik} L_{jk} F_{ij}$ for each normal vibration of $\text{CF}_2 = \text{CF}_2$ molecule.

	$\nu_1(\text{C}=\text{C} \text{ stretching})$	$\nu_2(\text{C}-\text{F} \text{ stretching})$
	$R_1 \begin{bmatrix} R_1 & R_2 & R_3 \\ 1.896 & & \\ -0.129 & 0.485 & \\ -0.084 & -0.056 & 0.219 \end{bmatrix}$	$\begin{bmatrix} R_1 & R_2 & R_3 \\ 0.032 & & \\ 0.013 & 0.298 & \\ -0.002 & 0.010 & 0.022 \end{bmatrix}$
	$\nu_3(\text{CF}_2 \text{ deformation})$	
A_g	$R_1 \begin{bmatrix} R_1 & R_2 & R_3 \\ 0.004 & & \\ 0.000 & 0.004 & \\ 0.002 & -0.003 & 0.083 \end{bmatrix}$	
	$\nu_4(\text{C}-\text{F} \text{ stretching})$	$\nu_5(\text{CF}_2 \text{ rocking})$
B_{1g}	$R_4 \begin{bmatrix} R_4 & R_5 \\ 0.990 & \\ -0.118 & 0.456 \end{bmatrix}$	$\begin{bmatrix} R_4 & R_5 \\ 0.034 & \\ 0.010 & 0.103 \end{bmatrix}$
	$\nu_6(\text{C}-\text{F} \text{ stretching})$	$\nu_7(\text{CF}_2 \text{ rocking})$
B_{2u}	$R_6 \begin{bmatrix} R_6 & R_7 \\ 1.024 & \\ -0.023 & 0.018 \end{bmatrix}$	$\begin{bmatrix} R_6 & R_7 \\ 0.000 & \\ -0.000 & 0.034 \end{bmatrix}$
	$\nu_8(\text{C}-\text{F} \text{ stretching})$	$\nu_9(\text{CF}_2 \text{ deformation})$
B_{3u}	$R_8 \begin{bmatrix} R_8 & R_9 \\ 0.774 & \\ -0.057 & 0.144 \end{bmatrix}$	$\begin{bmatrix} R_8 & R_9 \\ 0.013 & \\ 0.008 & 0.168 \end{bmatrix}$