

## VIBRATIONAL STATE ANALYSIS OF UNRELAXED BaI FROM THE REACTIONS Ba + CH<sub>3</sub>I AND Ba + CH<sub>2</sub>I<sub>2</sub>

P.J. DAGDIGIAN

*Department of Chemistry, The Johns Hopkins University,  
Baltimore, Maryland 21218, USA*

H.W. CRUSE

*Shell Research Ltd., Thornton Research Centre,  
PO Box 1, Chester CH1 3SH, UK*

and

R.N. ZARE

*Department of Chemistry, Columbia University,  
New York, New York 10027, USA*

Received 16 February 1976

The reactions Ba + CH<sub>3</sub>I → BaI + CH<sub>3</sub> and Ba + CH<sub>2</sub>I<sub>2</sub> → BaI + CH<sub>2</sub>I have been investigated by the method of laser-induced fluorescence. Excitation spectra are reported for BaI products formed under single-collision conditions in a "beam-gas" arrangement. The production of BaI for Ba + CH<sub>2</sub>I<sub>2</sub> is found to be a major reaction pathway with a cross section about twice that for Ba + CH<sub>3</sub>I. The relative vibrational populations show for both reactions bell-shaped distributions peaking close to  $v = 21$  for Ba + CH<sub>3</sub>I and  $v = 39$  for Ba + CH<sub>2</sub>I<sub>2</sub>. The corresponding average fraction of the total reaction exoergicity that appears as BaI vibration is  $\bar{f}_v = 0.18$  for Ba + CH<sub>3</sub>I and  $\bar{f}_v = 0.29$  for Ba + CH<sub>2</sub>I<sub>2</sub>. In the case of Ba + CH<sub>3</sub>I, an estimate for the average relative translational energy of the products, obtained from the primitive angular distribution measurements of Lin, Mims and Herm, can be combined with the average vibrational excitation of BaI to provide evidence that the internal excitation of the methyl radical exceeds that of BaI. A model is discussed which postulates an electron jump in the exit valley of the Ba + CH<sub>3</sub>I reaction to account for this feature of the reaction dynamics.

### 1. Introduction

The various combinations of the gas-phase Wurtz reaction †,



where A is an alkali atom, X a halogen atom, and R an alkyl group, were studied long ago in diffusion flames [2]. In the past decade or so, these reactions have received new attention since they can be investigated in

detail by molecular beam scattering techniques. In particular, K + CH<sub>3</sub>I is perhaps the most thoroughly studied molecular beam reaction [3] and may be properly termed a "touchstone" reaction. In addition to angular ‡ and velocity ¶ measurements of the products, there have been experiments on nonreactive scattering [6], magnetic deflection of the products [7], variation of the total reactive cross section with initial kinetic energy [8], and reactivity as a function of the orientation of the collision partners [9].

† The early beam experiments established the basic "rebound" character of the reaction [4].

¶ The most recent velocity analysis measurements have been performed by Rulis and Bernstein [5].

† In fact, eq. (1) is the first step of the Wurtz reaction,  $2M + 2RX \rightarrow RR + 2MX$ . See, for example, Roberts and Caserio [1].

Angular distributions of several alkaline earth analogs of (1) have recently been reported by Lin, Mims and Herm [10]. They used thermal crossed beams and mass spectrometric detection. In Ba + CH<sub>3</sub>I the BaI<sup>+</sup> signal peaks backward in the center of mass system, showing the same rebound character as A + CH<sub>3</sub>I. For the reaction Ba + CH<sub>2</sub>I<sub>2</sub>, the BaI<sup>+</sup> signal peaks forward in the center of mass system, again similar to the observed behavior for K + CH<sub>2</sub>I<sub>2</sub> and Cs + CH<sub>2</sub>I<sub>2</sub> [11]. However, Ba + CH<sub>2</sub>I<sub>2</sub> has a feature very different from the alkali analogs, namely, the formation of BaI<sub>2</sub> is energetically allowed. The ion fragmentation pattern of BaI<sub>2</sub>, especially when it is vibrationally excited, is almost exclusively BaI<sup>+</sup> †. Hence in the reaction Ba + CH<sub>2</sub>I<sub>2</sub> it is very difficult to distinguish the two possible products, BaI and BaI<sub>2</sub>, using mass spectrometry. Nevertheless, based on an analysis of their BaI<sup>+</sup> laboratory angular distributions, Lin et al. have suggested that the dominant reaction product they observe is BaI<sub>2</sub>.

We report here a study of the Ba + CH<sub>3</sub>I and Ba + CH<sub>2</sub>I<sub>2</sub> reactions using laser-induced fluorescence. In both cases, the BaI product is observed and the BaI vibrational state distribution is found to be markedly inverted, peaking at  $v \approx 21$  for Ba + CH<sub>3</sub>I and  $v \approx 39$  for CH<sub>2</sub>I<sub>2</sub>. Although we are unable to detect BaI<sub>2</sub> in the latter reaction, the formation of the BaI product appears to be a major pathway.

## 2. Experimental

The Ba + CH<sub>3</sub>I and CH<sub>2</sub>I<sub>2</sub> reactions were studied at Columbia in 1973; the Ba + CD<sub>3</sub>I reaction at Johns Hopkins in 1975. The interpretation of these results has awaited an accurate estimate for the BaI dissociation energy [14], which has only been obtained recently.

The apparatus employed in both cases does not differ significantly from that described in detail in our work on Ba + O<sub>2</sub> and Ba + CO<sub>2</sub> [15]. A barium beam effuses from an orifice in the source and passes through a slit into the scattering chamber, which is filled with alkyl iodide at pressures of  $(3-30) \times 10^{-5}$  torr

† It has been found that no parent peak is present in the mass spectra of CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub> [12]. Some parent peak is present for MgF<sub>2</sub>, while for the other magnesium dihalides, MgX<sub>2</sub> is formed predominantly [13]. Any internal excitation of BaI<sub>2</sub> would tend to lower the fraction of BaI<sub>2</sub><sup>+</sup> formed.

("beam+gas" arrangement). The output from a pulsed dye laser intersects the Ba beam in the scattering chamber, and the fluorescence is viewed by a photomultiplier (RCA 7265, S-20 photocathode). A PAR model 160 boxcar integrator (aperture 100 ns) is used to amplify and average the fluorescence signals. The output of the boxcar drives a stripchart recorder. The dye laser is scanned in wavelength to generate an excitation spectrum of the BaI product using the C<sup>2</sup>Π<sub>3/2</sub>-X<sup>2</sup>Σ<sup>+</sup> band system †. By varying the pressure we verify that there is no appreciable collisional relaxation of the product internal state distributions. As before, the laser power is reduced to minimize the effects of optical pumping so that the fluorescence intensity is proportional to laser power.

Commercial iodomethane (J.T. Baker) and diiodomethane (Matheson, Coleman and Bell) are used as reagents. The purity of the samples was checked with a 60 MHz proton nmr spectrometer. One serious problem was CH<sub>3</sub>I impurity in the CH<sub>2</sub>I<sub>2</sub> samples. Because of the disparate vapor pressures [17] (330 torr for CH<sub>3</sub>I versus 1 torr for CH<sub>2</sub>I<sub>2</sub> at 20°C), even 0.5% CH<sub>3</sub>I contamination in the CH<sub>2</sub>I<sub>2</sub> gives an appreciable contribution to the BaI signal. Accordingly, the CH<sub>2</sub>I<sub>2</sub> samples were purified by vacuum distillation, and only samples with no detectable CH<sub>3</sub>I proton nmr signal (< 0.05%) were used. The BaI spectra, taken with these samples of CH<sub>2</sub>I<sub>2</sub> show no discernible BaI attributable to CH<sub>3</sub>I (see also Results section). Iodomethane-*d*<sub>3</sub> is obtained from Aldrich (99 + atom % D stated purity). No effort was made to run the Ba + CD<sub>2</sub>I<sub>2</sub> reaction.

## 3. Results

### 3.1. Excitation spectra

Laser excitation of the C<sup>2</sup>Π-X<sup>2</sup>Σ<sup>+</sup> BaI band system which lies at 5300-5600 Å has been used for determination of the internal state distributions. Figs. 1-3 present scans of the variation of fluorescence intensity with laser wavelength for the Ba + CH<sub>3</sub>I, Ba + CD<sub>3</sub>I, and Ba + CH<sub>2</sub>I<sub>2</sub> reactions. The BaI bands for the Δ*v* = *v*'-*v* = 0 sequence of the <sup>2</sup>Π<sub>3/2</sub>-<sup>2</sup>Σ<sup>+</sup> subsystem are identified by comparison with previous band head measurements [18-20] (see also the appendix). In the

† For an example of a BaI excitation spectrum, see fig. 6 of [16].

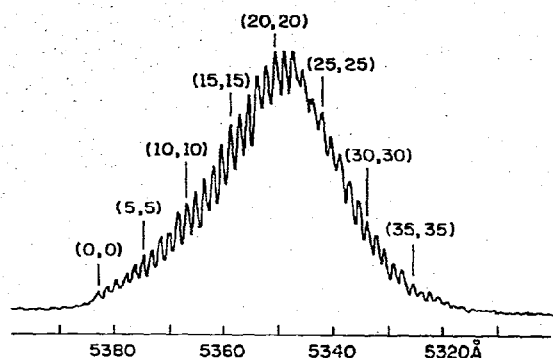


Fig. 1. BaI excitation spectrum of the  $C^2\Pi_{3/2} - X^2\Sigma^+ \Delta v = 0$  sequence for the Ba +  $CH_3I$  reaction. The numbering of the  $(v', v)$  band heads is indicated.

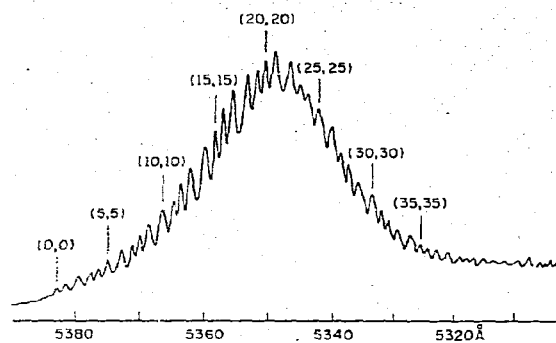


Fig. 2. BaI excitation spectrum of the  $C^2\Pi_{3/2} - X^2\Sigma^+ \Delta v = 0$  sequence for the Ba +  $CD_3I$  reaction.

Ba +  $CH_2I_2$  reaction although both BaI and BaI<sub>2</sub> products are energetically possible, all the bands observed in the present experiment are attributable to BaI. As seen in fig. 3, bands with  $v$  as high as 50 are present.

For low  $v$ , the  $\Delta v = 0$  sequence is by far the most intense. Indeed, for the previously studied Ba + HI reaction [16], in which only the vibrational levels  $0 \leq v \leq 23$  are populated, the  $\Delta v = 0$  sequence comprised about 95% of the total intensity. As can be inferred from the molecular constants derived in the appendix (see also table 3), the potential curves of the BaI electronic states are remarkably harmonic and very similar to one another. The dominance of the  $\Delta v = 0$  sequence also suggests that the curves run nearly parallel to one another. Accordingly, a reasonable assumption for the Franck-Condon factor (FCF) array is a delta function,  $q_{v',v} = \delta_{v',v}$ . As  $v$  increases, this assumption becomes progressively less applicable. Hence, the  $\Delta v = \pm 1$  and  $\pm 2$  sequences, as well as the  $\Delta v = 0$  sequence, have significant intensity in the present spectra. Nevertheless, by comparison of the intensities of the same  $v$  bands in different sequences, the delta function approximation is shown to be reasonable. For  $v$  levels as high as 40, fluorescence intensities excited in the  $\Delta v = 0$  sequence are found to be at least 3 times greater than the sum of the intensities from all  $\Delta v \neq 0$  bands. Since we have insufficient spectroscopic data available to calculate Franck-Condon factors for BaI, we will assume that this approximation applies to all levels observed. Hence, as shown previously [16], this implies that the  $\Delta v = 0$  band intensities

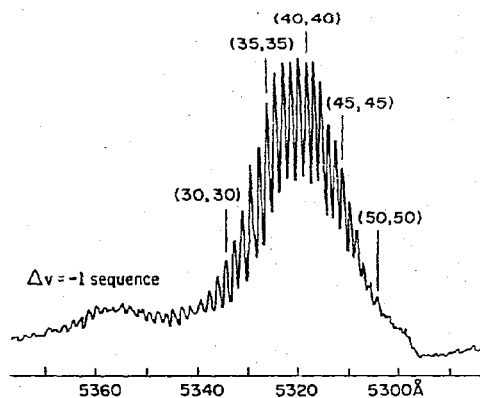


Fig. 3. BaI excitation spectrum of the  $C^2\Pi_{3/2} - X^2\Sigma^+ \Delta v = 0$  sequence for the Ba +  $CH_2I_2$  reaction. The shoulder marked " $\Delta v = -1$  sequence" is due to unresolved bands of this sequence. See text.

are proportional to vibrational populations.

The shoulder denoted in fig. 3 by " $\Delta v = -1$  sequence" is most likely not due to  $CH_3I$  impurity in the  $CH_2I_2$  sample, in spite of the fact that it lies at nearly the same wavelength as the low  $v$  bands of the  $\Delta v = 0$  sequence. This is ascertained by the different dependence of its intensity on laser power from that of the  $\Delta v = 0$  sequence. Since the extent of optical pumping is proportional to absorption coefficient and hence Franck-Condon factor  $q_{v',v}$ , this implies that the bands in the shoulder have significantly different  $q_{v',v}$  values

from those in the  $\Delta\nu = 0$  sequence and hence belong to another sequence.

Because of the small vibrational frequency and large dissociation energy [14], the  $\nu = 50$  level corresponds to only one-fourth of the ground state dissociation energy. It is not known into which atomic terms the BaI C state dissociates. However, the highest vibrational levels excited in this laser fluorescence study lie below the energy of the ground state separated atoms, Ba( $^1S_0$ ) + I( $^2P_{3/2}^0$ ). Thus, the termination of the  $\Delta\nu = 0$  sequence at high vibrational levels (see figs. 1–3) is not caused by photodissociation or predissociation of the excited state.

A search in the region 4400–5600 Å did not reveal any bands that could be ascribed to BaI<sub>2</sub>. We note, however, that the observation of no BaI<sub>2</sub> bands is not proof that only BaI is formed in the Ba + CH<sub>2</sub>I<sub>2</sub> reaction since the BaI<sub>2</sub> electronic spectrum is not known. In fact, the BaI<sub>2</sub> spectrum is expected to lie to the violet of the BaI spectrum since it has no unpaired electrons, unlike BaI.

### 3.2. Reaction energetics

We present here the necessary calculations required to determine the reaction exothermicities for Ba + CH<sub>3</sub>I and Ba + CH<sub>2</sub>I<sub>2</sub>. We can calculate  $D_{298}^{\circ}$ , the dissociation energies at 298 K, of the alkyl iodides by substituting heats of formation at 298 K,  $\Delta H_{298}^{\circ}$ , into the thermodynamic cycle,



so that

$$D_{298}^{\circ}(R-I) = \Delta H_{298}^{\circ}(R) + \Delta H_{298}^{\circ}(I) - \Delta H_{298}^{\circ}(RI). \quad (3)$$

For methyl iodide, we use the values  $+34.82 \pm 0.2$  [21],  $+25.537$  [21], and  $+3.29 \pm 0.28$  [22] kcal/mole for  $\Delta H_{298}^{\circ}$  of CH<sub>3</sub>, I, and CH<sub>3</sub>I, respectively, and obtain  $D_{298}^{\circ}(\text{CH}_3\text{-I}) = 57.1 \pm 0.3$  kcal/mole. For methylene iodide, we use  $\Delta H_{298}^{\circ}(\text{CH}_2\text{I}_2) = +28.37 \pm 1.0$  [22] and  $\Delta H_{298}^{\circ}(\text{CH}_2\text{I}) = +54 \pm 2$  kcal/mole, the average of 2 determinations [23, 24], and obtain  $D_{298}^{\circ}(\text{CH}_2\text{I-I}) = 51.2 \pm 2$  kcal/mole. These dissociation energies are converted to  $D_0^{\circ}$  with the use of tabulated ideal gas enthalpies [21, 22]:

$$D_{298}^{\circ}(R-I) - D_0^{\circ}(R-I) = [H_{298}^{\circ}(R) - H_0^{\circ}(R)] \\ + [H_{298}^{\circ}(I) - H_0^{\circ}(I)] - [H_{298}^{\circ}(RI) - H_0^{\circ}(RI)]. \quad (4)$$

Table 1  
Reaction energetics (in kcal/mole)

	Ba + CH <sub>3</sub> I → BaI + CH <sub>3</sub>	Ba + CH <sub>2</sub> I <sub>2</sub> → BaI + CH <sub>2</sub> I
Reactants		
$E_{\text{int}}$	1.1	1.7
$E_{\text{trans}}^a$	2.1	2.6
$E_{\text{tot}}$	3.2	4.3
Products:		
$\Delta D_0$	46	52
$E_{\text{tot}}$	50	56

<sup>a</sup>) Calculated using the most probable velocities of the reactants and a 90° intersection angle.

For CH<sub>2</sub>I, we use  $H_{298}^{\circ} - H_0^{\circ}$  given for CH<sub>3</sub>I [21]; this certainly is of sufficient accuracy, given the 2 kcal/mole uncertainty in  $\Delta H_{298}^{\circ}(\text{CH}_2\text{I})$ . We obtain  $D_0^{\circ}(\text{CH}_3\text{-I}) = 55.7 \pm 0.3$  and  $D_0^{\circ}(\text{CH}_2\text{I-I}) = 50.3 \pm 2$  kcal/mole.

The dissociation energy of BaI has long eluded quantitative determination. Dickson, Kinney, and Zare [14] discuss the available experimental data; they have used the Ba + I<sub>2</sub> chemiluminescent reaction to place the bound  $D_0^{\circ}(\text{BaI}) \geq 102 \pm 1$  kcal/mole, which we use here †.

Table 1 summarizes the average energy of the reactants and the energy available to the products. Here  $E_{\text{trans}}$ ,  $E_{\text{int}}$ , and  $E_{\text{tot}} = E_{\text{trans}} + E_{\text{int}}$  are the translational, internal, and total energy, respectively,  $\Delta D_0$  is the reaction exothermicity, i.e., the difference in product and reactant molecule dissociation energies, and  $E_{\text{tot}}' = E_{\text{tot}} + \Delta D_0$  is the total energy available to the products. The reaction pathway Ba + CH<sub>2</sub>I<sub>2</sub> → BaI<sub>2</sub> + CH<sub>2</sub> has not been included in table 1 since no BaI<sub>2</sub> has been observed in the present study. However, Lin et al. [10] estimate  $\Delta D_0$  to be about 70 kcal/mole for this pathway.

### 3.3. BaI internal energy distribution

In principle, the vibrational and rotational energy distributions can be obtained from the excitation spec-

† The use of this value for  $D_0^{\circ}(\text{BaI})$  changes in ref. [16] the Ba + HI reaction exoergicity from 1.26 to 1.48 eV and the average fraction of total energy appearing in product vibration from  $\bar{f}_v = 0.18$  to 0.15. The conclusion of ref. [16] are unaffected.

trum by computer simulation. In this procedure, a calculated excitation spectrum is constructed by assuming a population distribution for the internal states and convoluting it with the laser bandwidth function. Previously, BaX excitation spectra were analyzed for the Ba + HF and Ba + HCl reactions, in which the relative vibrational populations and a single rotational temperature were allowed to vary in order to obtain a best fit [16]. However, this procedure cannot be applied in the present instance because of a dearth of spectroscopic data.

The BaI rotational constants are not known, and indeed even the shading of the  $\Delta v = 0$  bands is undetermined [18]. The  $J$  value at which the band head occurs depends on the difference  $B_v' - B_v$ . However,  $B'$  is almost identical to  $B''$  so that the value of  $J$  at the head is very large and may vary significantly from band to band depending on the difference  $B_v' - B_v$  as a function of  $v$ . Consequently, the height of the band head measured with respect to either the baseline or to the envelope of valleys may not represent the true band intensity. This is further complicated by the extensive contributions of neighboring bands to the intensity at a given band head position. Finally, accurate Franck-Condon factors are not available so that we must resort to the delta function approximation described in section 3.1.

Even if we could overcome these difficulties to obtain internal state relative populations (number densities) from the spectra, there still remains the problem that relative rate constants (cross sections) are proportional to the flux of products, and not number densities. Unlike the previously studied Ba + HX reactions [16], the proportionality constant between flux and density, namely the product laboratory velocity, could vary significantly with internal state: The BaI velocities in the center-of-mass system are larger than the velocity of the center of mass for these reactions.

With all these problems in mind, we have nonetheless derived relative vibrational populations for the Ba + CH<sub>3</sub>I and Ba + CH<sub>2</sub>I<sub>2</sub> reactions from the excitation spectra (figs. 1–3). We have arbitrarily assumed that  $\Delta v = 0$  band intensities are proportional to the heights of the band heads above the envelope of valleys. Using the delta function approximation for the BaI FCFs (see section 3.1), we take these band intensities to be directly proportional to vibrational populations. The results of this crude analysis are displayed in fig. 4. In spite of the large number of approximations made,

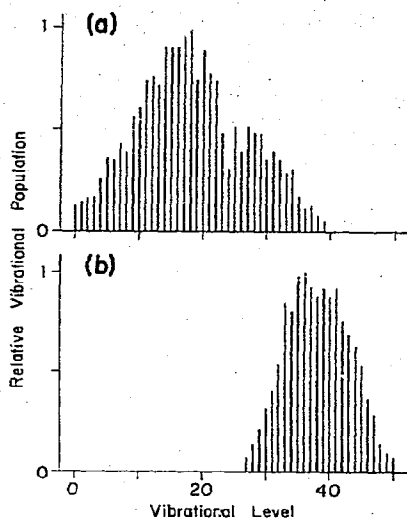


Fig. 4. Relative vibrational populations for (a) the Ba + CH<sub>3</sub>I and (b) the Ba + CH<sub>2</sub>I<sub>2</sub> reactions. The populations, which are normalized to the most probable level, have been obtained in an approximate manner as described in the text.

we believe that fig. 4 displays the qualitative features of the BaI vibrational state distributions. The populations can be seen to vary fairly smoothly from state to state. Moreover, the overall shapes are distinctly different from a Boltzmann (thermal) distribution but rather are bell-shaped †. We have chosen not to plot a Ba + CD<sub>3</sub>I distribution in fig. 4 since it differs insignificantly from that for Ba + CH<sub>3</sub>I.

We take the average energy appearing as BaI variation,  $\langle E'_{\text{vib}} \rangle$ , as the vibrational energy of the most probable level, assumed to be the level having the highest peak height above the baseline. Alternatively, one could take  $\langle E'_{\text{vib}} \rangle$  as the energy weighted over the relative vibrational populations shown in fig. 4. However, because of the many approximations employed to derive these populations, the simpler procedure seems adequate. For the Ba + CH<sub>3</sub>I and Ba + CH<sub>2</sub>I<sub>2</sub> reactions, the most probable vibrational levels are 21 and 39, respectively. Using the BaI molecular constants presented in table 3, this implies that  $\langle E'_{\text{vib}} \rangle$  is 8.8 kcal/mole for Ba + CH<sub>3</sub>I

† The Ba + CH<sub>3</sub>I reaction shows a possible hint of a bimodal distribution in the vibrational state populations of the BaI product, but this may be an artifact of the simple analysis employed here.

and 15.8 kcal/mole for Ba + CH<sub>2</sub>I<sub>2</sub>. Because the excitation spectrum for Ba + CD<sub>3</sub>I is essentially identical to that of the Ba + CH<sub>3</sub>I reaction, ( $E'_{\text{vib}}$ ) is the same for these two reactions.

The BaI rotational distributions are probably different in the Ba + CH<sub>3</sub>I and Ba + CH<sub>2</sub>I<sub>2</sub> reactions since the band heads are more prominent in the Ba + CH<sub>2</sub>I<sub>2</sub> reactions since the band heads are more prominent in the Ba + CH<sub>2</sub>I<sub>2</sub> excitation spectrum (fig. 3). However, because of a lack of spectroscopic information, we are unable to estimate  $E'_{\text{rot}}$ , the BaI product rotational energy, or even to establish for which reaction  $E'_{\text{rot}}$  is greater.

#### 3.4. Relative total reactive cross sections

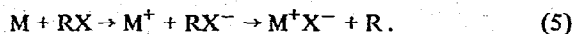
The relative total cross sections  $\sigma_r$  for formation of BaI product may be obtained by summing up the fluorescence intensity from all bands of the BaI C–X system. We find that the ratio of the cross section for formation of BaI by the Ba + CH<sub>2</sub>I<sub>2</sub> reaction to that for the Ba + CH<sub>3</sub>I reaction is 1.9. We have assumed that the calibration constant for the Bayard–Alpert type ionization gauge is the same for both CH<sub>3</sub>I and CH<sub>2</sub>I<sub>2</sub>. Although the Ba + CH<sub>2</sub>I<sub>2</sub> reaction may also cause the formation of BaI<sub>2</sub>, the present measurement of  $\sigma_r$  values indicates that the formation of BaI is an important reaction pathway for Ba + CH<sub>2</sub>I<sub>2</sub>.

## 4. Discussion

### 4.1 Ba + CH<sub>3</sub>I

A convenient interpretive framework for understanding the reactions of barium with the halomethanes is provided by their well-studied alkali analogs. In the case of methyl iodide, the outstanding characteristics of these analogous reactions include predominantly backward scattering of the salt product with respect to the incident direction of the atomic beam in the center-of-mass system [4], the conversion of a significant fraction of the total available reaction energy into product relative translational energy (~65% for the case of K + CH<sub>3</sub>I [3]), and relatively small cross sections compared to other alkali reactions. A simple explanation for these observations has been offered by Herschbach [25]. Most alkali reactions with halogen-

containing molecules are thought to proceed by an electron-jump model in which the valence electron of the alkali atom is transferred to the halogen-containing molecule in the neighborhood of the intersection between the covalent (M + RX) and ionic (M<sup>+</sup> + RX<sup>-</sup>) potential energy curves. The reaction then proceeds as an ion recombination



The crossing point  $R_c$  occurs at a distance given by

$$R_c(\text{\AA}) \approx 14.47 \text{ eV} / [\text{IP}(M) - \text{EA}(RX)] \quad (6)$$

where IP(M) is the ionization potential of M and EA(RX) the vertical electron affinity of (RX), both measured in eV. In the case of methyl iodide, EA(CH<sub>3</sub>I) is expected to be negative and the reactants must approach very close to one another before reaction can occur. This provides an explanation for both the small cross section and the rebound character of the MX angular distribution.

As Herschbach has stressed [25, 26], the recoil energies can be explained by comparison with the photodissociation dynamics of CH<sub>3</sub>I. The unstable CH<sub>3</sub>I<sup>-</sup> formed in the alkali reaction after the electron jump is assumed to decay in a manner similar to the mode of decomposition of optically excited CH<sub>3</sub>I\*, namely by release of the energy predominantly into fragment recoil rather than internal excitation, as shown by the photofragment studies of Riley and Wilson [27]. The lowest unfilled molecular orbital in the haloalkanes are formed from the out-of-phase overlap of an sp<sup>3</sup> hybrid orbital of the carbon atom (C) and a p orbital of the halogen atom (X). They are of the anti-bonding type  $\sigma^*$  with a node between the C–X bond. In the electronic transitions of lowest energy, a non-bonding p electron bound to the halogen atom is excited into the lowest  $\sigma^*$  orbital, causing the molecule to dissociate. In the electron-jump model, the electron transferred to the RX molecule enters the same  $\sigma^*$  orbital.

Since the ionization potential of Ba is intermediate between that of Na and Li, one might expect the reaction dynamics for Ba + CH<sub>3</sub>I to be similar to those of Na + CH<sub>3</sub>I [28] and Li + CH<sub>3</sub>I [29], for which crossed-beam data are available. Indeed, all these reactions show rebound character in the angular distribution of the salt product. Table 2 lists the results from these crossed-beam experiments, as well as that for the well-

Table 2  
Summary of crossed-beam experiments for several  
 $M + \text{CH}_3\text{I} \rightarrow \text{MI} + \text{CH}_3$  reactions (energies in kcal/mole)

M	IP(M) a)	$E_{\text{tot}}$ b)	$\Delta D_0$ c)	$E'_{\text{tot}}$	$\langle E'_{\text{trans}} \rangle$	Ref.
Ba	5.210	4	46	50	~13 d)	[10]
Li	5.390	3	28	31	~15 d)	[29]
Na	5.138	3	16	19	~15 d)	[28]
K	4.339	4	23	27	16	[5]

a) Atomic ionization potentials (in eV) are taken from [30].

b) Total energy, both translational and internal, of the reactants.

c) Alkali iodide dissociation energies  $D_0^\circ$  are taken from [31].

d) These values for the average product relative translational energy  $\langle E'_{\text{trans}} \rangle$  are obtained in "primitive" scattering experiments, in which there was no velocity analysis of the products.

studied  $\text{K} + \text{CH}_3\text{I}$  reaction. All these reactions, while having greatly different exothermicities, exhibit similar average product recoil energies  $\langle E'_{\text{trans}} \rangle$ . However, as shown by Rulis and Bernstein [32] for  $\text{K} + \text{CH}_3\text{I}$ , the value for  $\langle E'_{\text{trans}} \rangle$  determined from a so-called "primitive" crossed-beam experiment (10 kcal/mole [33]) is significantly in error compared to a more refined cross-beam experiment in which the velocity of the products is analyzed (16 kcal/mole). This difficulty with "primitive" experiments is expected to be most pronounced for reactions with unfavorable kinematics, i.e., in which the mass of the detected product is much greater than that of the other product. Thus we are led to consider the result  $\langle E'_{\text{trans}} \rangle = 13 \pm 3$  kcal/mole for  $\text{Ba} + \text{CH}_3\text{I}$  by Lin et al. [10] as a lower limit, which may be smaller than the true value of  $\langle E'_{\text{trans}} \rangle$  by, perhaps, as much as a factor of two.

Despite these superficial similarities between the barium and alkali reactions with methyl iodide, some striking differences appear when we examine the extent of internal excitation of the product methyl radical,  $E'_{\text{int}}(\text{CH}_3)$ . In their review of the  $\text{K} + \text{CH}_3\text{I}$  reaction, Bernstein and Rulis [3] estimate that  $\langle E'_{\text{int}}(\text{KI}) \rangle \approx 11$  kcal/mole and  $\langle E'_{\text{int}}(\text{CH}_3) \rangle \leq 4$  kcal/mole. This degree of  $\text{CH}_3$  excitation correlates well with the energy found in the  $\text{CH}_3$  fragment (4 kcal/mole) following photodissociation of  $\text{CH}_3\text{I}$  [27], in accordance with Herschbach's analogy. The extent of  $\text{CH}_3$  excitation in the  $\text{Ba} + \text{CH}_3\text{I}$  reaction may be obtained by combining our data on the excitation of BaI with the product recoil energy estimate given by

Lin et al. To obtain a lower bound for  $\langle E'_{\text{int}}(\text{CH}_3) \rangle$ , we double the estimate of the product recoil energy and use the value  $\langle E'_{\text{trans}} \rangle = 26$  kcal/mole. From the present experiment (see section 3.3), we obtain  $\langle E'_{\text{int}}(\text{BaI}) \rangle = 9$  kcal/mole, assuming that the rotational excitation of BaI is small. Subtraction from the value of  $E'_{\text{tot}}$  given in table 1 then yields the result  $\langle E'_{\text{int}}(\text{CH}_3) \rangle \gtrsim 15$  kcal/mole. This energy is not only significantly greater than for the  $\text{K} + \text{CH}_3\text{I}$  reaction or for  $\text{CH}_3\text{I}$  photodissociation, but it is also greater than that predicted by a simple impulsive model. Bass and Pimentel [34] have estimated that if  $\text{CH}_3$  were left in its tetrahedral configuration as a nascent product, then it would have about 10 kcal/mole of vibrational energy as it transforms to its equilibrium planar or near planar structure [35, 36].

We have attempted to gauge further the extent of methyl excitation by comparing the BaI vibrational distribution from the isotopic reactions  $\text{Ba} + \text{CH}_3\text{I}$  and  $\text{Ba} + \text{CD}_3\text{I}$ . The vibrational and rotational frequencies of  $\text{CH}_3$  and  $\text{CD}_3$  are quite different. However, as pointed out in section 3.3, the BaI distributions are essentially the same. Unfortunately, this result does not allow us to conclude much about the nature of the methyl excitation. Only about 20% of the available energy appears as BaI internal excitation. Hence, shifts of the remaining 80% of the energy between  $E'_{\text{trans}}$  and  $E'_{\text{int}}(\text{methyl})$  are not ruled out.

The  $\text{Ba} + \text{CH}_3\text{I}$  reaction seems to be rather unusual in that more internal excitation appears in the "old bonds" of the methyl radical than in the "new bond" of BaI. We are tempted to speculate on the cause of this apparently large amount of product methyl excitation. However, such speculations are hampered at the present time by the fact that the disposal of the reaction energy is not firmly established. Additional experimental work, such as product velocity analysis like that performed for  $\text{K} + \text{CH}_3\text{I}$  [32] or measurement of the angular distribution of BaI internal states (see, for example, [37, 38]), is needed so that the product recoil energy can be determined. In addition, an estimate of the product BaI rotational energy is also required. Nevertheless, trajectory studies, such as those of Bunker and Goring-Simpson [39] on  $\text{Rb} + \text{CH}_3\text{I}$ , would be of interest to identify features of the potential surface which can cause substantial methyl excitation.

It would seem that the value of  $E'_{\text{int}}(\text{CH}_3)$  requires

substantial repulsion between the leaving BaI product and the "umbrella" of three methyl hydrogens about the central carbon atom. A possible explanation for this behavior might be a late curve crossing between the covalent potential surface of BaI + CH<sub>3</sub> and the ionic potential surface of BaI<sup>+</sup> + CH<sub>3</sub><sup>-</sup> in the exit valley of the reaction surface. The ionization potential of BaI is thought to be less than that of Ba [40], unlike the case of IP(KI) compared to IP(K). On the other hand, the electron affinity of the methyl radical is positive and is thought to have the approximate value of 1.08 eV [41]. The structure of BaI<sup>+</sup> is very similar to that of BaI, as is seen from the fact that the excited states of BaI are all Rydberg states whose shape and internuclear spacing are almost the same as the ground state. Indeed, this accounts for the dominance of the  $\Delta v = 0$  sequence in absorption and emission. In contrast, there is a very large geometry change between CH<sub>3</sub><sup>-</sup> and CH<sub>3</sub>. The CH<sub>3</sub><sup>-</sup> anion is isoelectronic to NH<sub>3</sub> and is expected to be pyramidal [42]. We then speculate that as BaI<sup>+</sup> + CH<sub>3</sub><sup>-</sup> switch to BaI + CH<sub>3</sub> the "umbrella" of methyl hydrogens "snap open", causing a large degree of internal excitation to appear in the "old bonds" of the CH<sub>3</sub> radical. It is inviting to consider the possibility that the Ba + CH<sub>3</sub>I reaction proceeds by a double electron jump, in analogy to the reaction of K<sub>2</sub> + CH<sub>3</sub>I [43], but it does not seem prudent to continue this line of reasoning here without more experimental evidence.

#### 4.2. Ba + CH<sub>2</sub>I<sub>2</sub>

The analogy with alkali reactions is also convenient for a discussion of the Ba + CH<sub>2</sub>I<sub>2</sub> reaction. The reactions K + CH<sub>2</sub>I<sub>2</sub> and Cs + CH<sub>2</sub>I<sub>2</sub> have been studied by crossed beams by Entemann at thermal energies and K + CH<sub>2</sub>I<sub>2</sub> with initial kinetic energies of 5–6 kcal/mole by Lin, Mascord and Grice, who used a supersonic potassium atom beam [11]. The reaction dynamics appear to be quite similar to the alkali–I<sub>2</sub> reactions, in which the alkali iodide is scattered predominantly in the forward direction with only a small amount of the reaction energy converted into product recoil †.

† Product velocity analysis of these reactions [44] shows that, on the average, only about 12 and 6% of the available energy appear as product recoil for K + CH<sub>2</sub>I<sub>2</sub> and Cs + CH<sub>2</sub>I<sub>2</sub>, respectively.

These stripping-type reactions are characterized by a large value of  $R_c$ , the covalent-ionic curve crossing radius, which results from the substantial electron affinity of I<sub>2</sub>. Hence, this suggests that CH<sub>2</sub>I<sub>2</sub> has a more positive vertical electron affinity than CH<sub>3</sub>I, in agreement with the trends from thermal electron attachment studies [45], and that this significantly alters the dynamics of the Ba + CH<sub>2</sub>I<sub>2</sub> reaction as compared to Ba + CH<sub>3</sub>I.

As indicated by fig. 4, the average product BaI vibrational energy for Ba + CH<sub>2</sub>I<sub>2</sub> is about twice as large as that for Ba + CH<sub>3</sub>I. This increase is in accord with the expected transition from rebound toward stripping dynamics. Moreover, it is clear from these inverted distributions that the dynamics involve direct collisions.

An additional complication for the CH<sub>2</sub>I<sub>2</sub> reaction arises because of the divalence of Ba. The formation of BaI<sub>2</sub> is an allowed reaction pathway. This feature causes an ambiguity in the analysis of the mass spectrometric crossed-beam study of Lin et al. [10] since the observed BaI<sup>+</sup> signal could arise from either BaI or BaI<sub>2</sub> products or both. If one assumes that only BaI product is formed, then Lin et al. show that the BaI<sup>+</sup> angular distribution is consistent with a product recoil energy of 1 kcal/mole or less. In this case, the kinematics are not nearly as unfavorable as for the CH<sub>3</sub>I reaction since the products (BaI and CH<sub>2</sub>I) differ only by a factor of 2 in mass. If on the other hand, formation of BaI<sub>2</sub> were the only significant pathway, then  $\langle E'_{trans} \rangle \approx 25$  kcal/mole. Lin et al. suggest that BaI<sub>2</sub> product is predominantly observed in their experiment since a recoil energy of only 1 kcal/mole seems very unlikely for a reaction with over 50 kcal/mole exoergicity. The present results show, however, that the formation of BaI product is an important reaction pathway.

Perhaps the most plausible explanation of the crossed-beam results is that BaI<sub>2</sub> product was indeed the only product observed since the kinematics would strongly discriminate against mass spectrometric observation of BaI because of its very large center-of-mass recoil velocity compared to that for BaI<sub>2</sub> [46]. This difference would cause BaI<sub>2</sub> to be closer to the detector scan plane (which is the plane of the incident beams).

Whatever the interpretation is for these crossed-beam results, the present experiment indicates that of the total available energy (56 kcal/mole) for the path-



way  $\text{Ba} + \text{CH}_2\text{I}_2 \rightarrow \text{BaI} + \text{CH}_2\text{I}$ , about 40 kcal/mole appears as  $\text{CH}_2\text{I}$  internal excitation, relative product translational energy, and also perhaps BaI rotational excitation. It seems likely that a significant fraction of this energy would appear as  $\text{CH}_2\text{I}$  excitation, as much as or more than  $\text{CH}_3$  excitation in the  $\text{Ba} + \text{CH}_3\text{I}$  reaction. Thus it again appears that more internal excitation may be in the "old bonds" of the iodomethyl radical than in the "new bond" of the barium monoiodide radical.

The small amount of energy that appears as BaI vibrational excitation differentiates the  $\text{Ba} + \text{CH}_2\text{I}_2$  reaction from a typical stripping reaction, such as  $\text{K} + \text{Dr}_2$ . From measurements of the velocity distribution [47, 48] and rotational excitation [49] of the KBr product, the KBr vibrational energy  $E'_{\text{vib}}$  (KBr) peaks at about 43 kcal/mole, out of a total reaction energy of about 45 kcal/mole. Indeed, as early diffusion flame studies [2] and later molecular beam experiments [50] showed, there is sufficient vibrational energy to excite alkali atoms electronically by a chemical exchange process,  $\text{KBr}^\dagger + \text{Na} \rightarrow \text{K}^* + \text{NaBr}$ .

In contrast, the product BaI vibrational energy for  $\text{Ba} + \text{CH}_2\text{I}_2$  amounts to only ~29% of the available energy and the supposedly indifferent  $\text{CH}_2\text{I}$  spectator is likely in fact to be highly internally excited. Clearly, simple stripping dynamics do not apply here. However, it is unclear to what extent the difference is caused by a change in the curve crossing radius or by the complicating features pertaining to the divalence of Ba. The latter could manifest itself in two ways. First, the departing BaI radical may, in some cases, tug on the remaining I atom of the  $\text{CH}_2\text{I}$  radical. Secondly, there may be once again a late curve crossing in the exit channel between  $\text{BaI}^+ + \text{CH}_2\text{I}^-$  and  $\text{BaI} + \text{CH}_2\text{I}$ , causing the  $\text{CH}_2\text{I}$  to become internally excited as the BaI radical departs. The geometry change between  $\text{CH}_2\text{I}^-$  and  $\text{CH}_2\text{I}$  would be expected to cause rotational as well as vibrational excitation of the  $\text{CH}_2\text{I}$  product, since the monohalomethyl radical is thought to be nearly planar ‡.

‡ There is an interesting correlation with the photodissociation dynamics of  $\text{CH}_2\text{I}_2$ . Once again an  $n \rightarrow \pi^*$  transition causes the molecule to dissociate [51]. Photofragment spectroscopy [52] shows that about 90% of the available energy appears as internal excitation of the  $\text{CH}_2\text{I}$  fragment, considerably more than for the photodissociation of  $\text{CH}_3\text{I}$ , and of this energy approximately 40% goes into rotational excitation of the  $\text{CH}_2\text{I}$ .

### 4.3. Comparison with other Ba + RX reactions

It would appear that two general features of the reactions of Ba with organic halides studied thus far as well as with the hydrogen halides [16, 53] are: (1) the formation of strongly inverted bell-shaped vibrational population distributions of the BaX product; and (2) the relatively small fraction of the total reaction energy that appears as excitation of the newly formed BaX bond. Just as in the case with the hydrogen halides, it should be emphasized that a plot of the surprisal [54] for the BaX vibrational distribution is not linear, but shows marked curvature for this class of reactions involving covalent-ionic curve crossings †. However, the second feature concerning the preference for energy disposal into "old bonds" is not true for all Ba + RX reactions. As recently shown by Schultz, Schmidt, and Siegel [56], about 75% of the available energy appears as BaCl vibration in the  $\text{Ba} + \text{CCl}_4$  reaction, although here once again the BaCl vibrational distribution is strongly inverted and bell-shaped. A partial explanation for this behavior may be that the structure of  $\text{CCl}_3$  is pyramidal [57, 58] so that an ionic-covalent crossing of  $\text{BaCl}^+ + \text{CCl}_3^-$  and  $\text{BaCl} + \text{CCl}_3$  does not strongly excite the  $\text{CCl}_3$  radical. It seems then that a comparative study of alkaline earth and RX reactions will be a fruitful area for future work. We may look forward to a better understanding of the dynamics of the present reactions as future experiments reveal systematic trends and determine more precisely the disposal of the total reaction energy.

### Acknowledgement

This work was supported in part by the U.S. Army Research Office and the National Science Foundation. Acknowledgement is also made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

† Levine [55] has asserted that the vibrational surprisal plot for  $\text{Ba} + \text{HCl}$  may be made linear by explicitly including the constraint that the fractional conversion of energy into product vibration  $\bar{f}_v$  is small. However, we do not understand why such a constraint should be applied since linearity is not a necessary characteristic of the information-theoretic approach.

### Appendix: Molecular constants of the BaI C-X band system

Even though the band spectrum of BaI was observed many years ago by Olmsted [59] and Walters and Barratt [60], only recently has it been possible to derive vibrational constants from band head measurements. Mesnage [18] was able to observe in the green 20 bands in two separate sequences with a doublet spacing of  $755 \text{ cm}^{-1}$ . Barrow, in the spectroscopic compilation edited by Rosen [61], reports unpublished analyses by Morgan and Barrow for the  $C^2\Pi-X^2\Sigma^+$  system in the green and for the ultraviolet  $D^2\Sigma^+-X^2\Sigma^+$  and  $E^2\Sigma^+-X^2\Sigma^+$  systems. However, the highest vibrational level observed in these studies was  $v'' \approx 13$  [62], so that extrapolation to the  $v'' = 50$  level, which was observed in the present experiment, cannot be made with confidence. More recently, Patel and Shah [19] have investigated these systems in emission. Patel [20] has kindly provided us with individual band head measurements. For the C-X system, in particular, some 285 band head wavelengths, with  $v''$  as high as 60, have been measured and vibrational assignments made.

We have performed a linear least squares fit to Patel's C-X band head measurements to obtain vibrational constants for both the ground and excited states. We find that it is necessary to include only the leading anharmonic correction to the vibrational spacings in both states, i.e.,  $G(v) = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2$ , in order to reproduce the experimental frequency to better than  $1 \text{ cm}^{-1}$  in most cases. As before when we estimated BaX molecular constants in our Ba + HX study [16], we force  $\omega_e'$  and  $\omega_e x_e'$  to be the same in both the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  sublevels by allowing a linear variation with  $(v + \frac{1}{2})$  in the  $C^2\Pi$  spin-orbit coupling constant  $A_v$ , i.e.,  $A_v = A_e + a_e(v + \frac{1}{2})$ . The vibrational constants found in this manner are listed in table 3, where  $T_e'$  is the common band origin.

The BaI vibrational constants we previously determined [16] in a similar manner can be seen to differ significantly from the present values. In that study, we did not have available extensive spectral measurements of the C-X system. Therefore we used the data of Reddy and Rao [63] for the D-X system to obtain ground state constants and then employed the data of Mesnage [18] for the C-X  $\Delta v = 0$  sequences to get excited state parameters. However, comparison of

Table 3  
Spectroscopic constants (in  $\text{cm}^{-1}$ ) for the BaI  $C^2\Pi-X^2\Sigma^+$  system <sup>a)</sup>

$X^2\Sigma^+$	$\omega_e''$	152.299(9)
	$\omega_e x_e''$	0.270297(4)
$C^2\Pi$	$T_e'$	18 191.2(33)
	$\omega_e'$	150.049(8)
	$\omega_e x_e'$	0.274821(3)
	$A_e$	754.93(5)
	$a_e$	0.20735(9)

<sup>a)</sup> The band head wavenumber of the  $(v', v'')$  band in the  $C^2\Pi\Omega-X^2\Sigma^+$  subsystem is given by

$$\nu = T_e' + [A_e + a_e(v' + \frac{1}{2})] \Lambda\Sigma + \omega_e'(v' + \frac{1}{2}) - \omega_e x_e'(v' + \frac{1}{2})^2 - \omega_e''(v'' + \frac{1}{2}) + \omega_e x_e''(v'' + \frac{1}{2})^2.$$

The numbers in parentheses are  $1\sigma$  of the fit in units of the last quoted digit.

the measurements of Reddy and Rao with the more extensive work of Patel shows that the former work is in error. The spectral dispersion used by Reddy and Rao was very low, and hence many individual bands in a sequence were not resolved. Moreover, the results of Patel substantially agree with those reported by Rosen [61] for the BaI C-X, D-X, and E-X systems as well as those communicated to us by Barrow [62]. The changes in the BaI molecular constants from those reported in our Ba + HX study do not significantly affect any of the conclusions reached in that paper.

### References

- [1] J.D. Roberts and M.C. Caserio, *Basic Principles of Organic Chemistry* (Benjamin, New York, 1965) pp. 345, 346.
- [2] M. Polanyi, *Atomic Reactions* (Williams and Norgate, London, 1932).
- [3] R.B. Bernstein and A.M. Rulis, *Faraday Discussions Chem. Soc.* 55 (1973) 293.
- [4] D.R. Herschbach, G.H. Kwei and J.A. Norris, *J. Chem. Phys.* 34 (1961) 1842; D.R. Herschbach, *Discussions Faraday Soc.* 33 (1962) 149.
- [5] A.M. Rulis and R.B. Bernstein, *J. Chem. Phys.* 57 (1972) 5497.
- [6] E. Hundhausen and H. Pauly, *Z. Physik* 187 (1965) 305; J.R. Airey, E.F. Greene, G.P. Reck and J. Ross, *J. Chem. Phys.* 46 (1967) 3295; R.M. Harris and J.F. Wilson, *J. Chem. Phys.* 54 (1971) 2088.
- [7] R.R. Herm, R.J. Gordon and D.R. Herschbach, *J. Chem. Phys.* 42 (1964) 2218;

- R.J. Gordon, R.R. Herm and D.R. Herschbach, *J. Chem. Phys.* **49** (1968) 2684;  
D.D. Parrish and R.R. Herm, *J. Chem. Phys.* **54** (1971) 2518.
- [8] M.E. Gersh and R.B. Bernstein, *J. Chem. Phys.* **55** (1971) 4661; **56** (1972) 6131.
- [9] P.R. Brooks and E.M. Jones, *J. Chem. Phys.* **45** (1966) 3449;  
R.J. Beuhler, Jr., R.B. Bernstein and K.H. Kramer, *J. Am. Chem. Soc.* **88** (1966) 5331;  
R.J. Beuhler, Jr. and R.B. Bernstein, *Chem. Phys. Letters* **2** (1968) 166; **3** (1969) 118;  
R.J. Beuhler, Jr. and R.B. Bernstein, *J. Chem. Phys.* **51** (1969) 5305;  
P.R. Brooks, *Faraday Discussions Chem. Soc.* **55** (1973) 299;  
G. Marcelin and P.R. Brooks, *ibid.*, 318.
- [10] S.M. Lin, C.A. Mims and R.R. Herm, *J. Phys. Chem.* **77** (1973) 569.
- [11] E.A. Entemann, *J. Chem. Phys.* **55** (1971) 4872;  
S.M. Lin, D.J. Mascord and R. Grice, *Mol. Phys.* **28** (1974) 975.
- [12] D.L. Hildenbrand and E. Murad, *J. Chem. Phys.* **43** (1965) 1400;  
G.D. Blue, J.W. Green, R.G. Bautista and J.L. Margrave, *J. Phys. Chem.* **67** (1963) 877;  
J.W. Green, G.D. Blue, T.C. Ehlert and J.L. Margrave, *J. Chem. Phys.* **41** (1964) 2245.
- [13] J. Berkowitz and J.R. Marquart, *J. Chem. Phys.* **37** (1962) 1853.
- [14] C.R. Dickson, J.B. Kinney and R.N. Zare, *Chem. Phys.* **15** (1976) 243.
- [15] P.J. Dagdigian, H.W. Cruse, A. Schultz and R.N. Zare, *J. Chem. Phys.* **61** (1974) 4450.
- [16] H.W. Cruse, P.J. Dagdigian and R.N. Zare, *Faraday Discussions Chem. Soc.* **55** (1973) 277.
- [17] R.C. Weast, ed., *CRC Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, Ohio, 1973); *Merck Index* (Merck & Co., Rahway, N.J., 1960) 7th Ed.
- [18] P. Mesnage, *Ann. Phys. (Paris)* **11** (12) (1939) 5.
- [19] M.M. Patel and N.R. Shah, *Ind. J. Pure Appl. Phys.* **8** (1970) 681.
- [20] M.M. Patel, private communication (1975).
- [21] JANAF Thermochemical Tables, NSRDS-NBS 37 (U.S. Government Printing Office, Washington, D.C., 1971).
- [22] S.A. Kudchadker and A.P. Kudchadker, *J. Phys. Chem. Ref. Data* **4** (1975) 457.
- [23] S. Furuyama, D.M. Golden and S.W. Benson, *Int. J. Chem. Kinetics* **1** (1969) 283.
- [24] J.J. DeCorpo, D.A. Bafus and J.L. Franklin, *J. Chem. Thermo.* **3** (1971) 125.
- [25] D.R. Herschbach, *Adv. Chem. Phys.* **10** (1966) 319.
- [26] D.R. Herschbach, *Faraday Discussions Chem. Soc.* **55** (1973) 233.
- [27] S.J. Riley and K.R. Wilson, *Faraday Discussions Chem. Soc.* **53** (1972) 132.
- [28] J.H. Birely, E.A. Entemann, R.R. Herm and K.R. Wilson, *J. Chem. Phys.* **51** (1969) 5461.
- [29] D.D. Parrish and R.R. Herm, *J. Chem. Phys.* **54** (1971) 2518.
- [30] C.E. Moore, NSRDS-NBS 35, Vols. I-III (U.S. Government Printing Office, Washington, D.C., 1971).
- [31] B. de B Darwent, NSRDS-NBS 31 (U.S. Government Printing Office, Washington, D.C., 1970).
- [32] A.M. Rulis and R.B. Bernstein, *J. Chem. Phys.* **57** (1972) 5497.
- [33] E.A. Entemann and D.R. Herschbach, *Discussions Faraday Soc.* **44** (1967) 289.
- [34] C.D. Bass and G.C. Pimentel, *J. Amer. Chem. Soc.* **83** (1961) 3754.
- [35] G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966) pp. 513-515.
- [36] M. Karplus, *J. Chem. Phys.* **30** (1959) 15.
- [37] P.J. Dagdigian and R.N. Zare, *J. Chem. Phys.* **61** (1974) 2464.
- [38] G.P. Smith and R.N. Zare, *J. Chem. Phys.*, **64** (1976) 2632.
- [39] D.L. Bunker and E.A. Goring-Simpson, *Faraday Discussions Chem. Soc.* **55** (1973) 93.
- [40] K.S. Krasnov, *Teplotfizika Vysokikh Temperatur* **3** (1965) 927 [English transl: *High Temperature* **3** (1965) 865].
- [41] J.L. Franklin and P.W. Harland, *Ann. Rev. Phys. Chem.* **25** (1974) 485.
- [42] A.D. Walsh, *J. Chem. Soc.* (1953) 2296, 2301.
- [43] S.M. Lin, D.J. Mascord and R. Grice, *Mol. Phys.* **28** (1974) 957.
- [44] S.J. Riley, private communication (1976).
- [45] W.E. Wentworth, R. George and H. Keith, *J. Chem. Phys.* **51** (1969) 1791.
- [46] R.R. Herm, private communication (1973).
- [47] A.E. Grosser and R.B. Bernstein, *J. Chem. Phys.* **43** (1965) 1140.
- [48] J.H. Birely and D.R. Herschbach, *J. Chem. Phys.* **44** (1966) 1690.
- [49] C. Maltz and D.R. Herschbach, *Discussions Faraday Soc.* **44** (1967) 176.
- [50] M.C. Moulton and D.R. Herschbach, *J. Chem. Phys.* **44** (1966) 3010.
- [51] M. Kawasaki, S.J. Lee and R. Bersohn, *J. Chem. Phys.* **63** (1975) 809.
- [52] S.J. Riley, Abstracts - 12th International Symposium on Free Radicals, Laguna Beach (January, 1976).
- [53] J.G. Pruett and R.N. Zare, *J. Chem. Phys.*, **64** (1976) 1774.
- [54] R.B. Bernstein and R.D. Levine, *Adv. in Atomic and Molecular Physics* **11** (1975) 215.
- [55] R.D. Levine, *Faraday Discussions Chem. Soc.* **55** (1973) 310.
- [56] A. Schultz, W. Schmidt and A. Siegel, in: *Electronic and Atomic Collisions: Abstracts of Papers of the IX ICPEAC*, eds. J.S. Risley and R. Geballe (Univ. Washington Press, Seattle, 1975) p. 345.

- [57] R.C. Ivey, P.D. Schulze, T.L. Leggett and D.A. Kohl, *J. Chem. Phys.* 60 (1974) 3174.  
[58] G.A. Carlson and G.C. Pimentel, *J. Chem. Phys.* 44 (1966) 4053.  
[59] C.M. Olmsted, *Z. Wiss. Photogr.* 4 (1906) 255.  
[60] O.H. Walters and S. Barratt, *Proc. Roy. Soc.* 118 (1928) 120.

- [61] B. Rosen, ed., *Spectroscopic Data Relative to Diatomic Molecules* (Pergamon, Oxford, 1970).  
[62] R.F. Barrow, private communication (1975).  
[63] B.R.K. Reddy and P.T. Rao, *J. Phys. B* 3 (1970) 1008.