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## ADVERTISEMENT



# Laser fluorescence study of ytterbium plus halomethane reactions

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The reactions of ytterbium (Yb) with a series of halomethanes (RX) have been studied in a beam plus gas arrangement. The unrelaxed YbX products are detected by cw tunable dye laser excitation. Prominent sequences belonging to the YbX ( $A^2\Pi_{1/2} - X^2\Sigma^+$ ) band systems are readily identified in the region 5350-6450 Å. The vibrational state distributions exhibited by the YbX products are characteristically bell-shaped, suggesting a direct reaction mechanism. Moreover, the fraction of energy released into YbX product vibration is found to increase with the reaction excergicity and with the degree of halogenation in RX. These systematic trends in the energy partitioning are correlated with recent results from the well-studied alkali and alkaline-earth analogs.

#### I. INTRODUCTION

Laser-induced fluorescence  $(LIF)^{1/2}$  has proven to be an extremely powerful technique for probing the internal excitation of nascent reaction products.<sup>3</sup> Recent applications of this method have yielded a wealth of spectroscopic and dynamical information on various classes of reactions, notably the alkaline earth metal plus hydrogen halide<sup>4-6</sup> and halomethane<sup>7-9</sup> systems, and several metal atom oxidation reactions.<sup>10-14</sup> In this paper we report on the first detection of ytterbium monohalides (YbX) by LIF under molecular beam conditions.<sup>15</sup> The YbX products are generated in a beam plus gas arrangement by the reactions of Yb with a series of halomethanes.

A number of recent studies<sup>16,17</sup> have alluded to the close analogy between the spectroscopic properties of YbX and those of the alkaline-earth monohalides. Reactive scattering<sup>17</sup> and chemi-ionization<sup>19</sup> studies have also revealed a very striking resemblance between the Yb and alkaline-earth atom plus halogen systems. In our present investigations we hope to gain further insight into the energy partitioning in these classes of M + RX reactions. Useful "by-products" from our studies include a determination of lower bounds for the dissociation energies of YbX and a derivation of vibrational constants for the YbX  $(A^2\Pi_{1/2}-X^2\Sigma^*)$  band systems from the LIF spectra. In this paper we shall focus on the dynamical information deduced from our studies. The spectroscopic data will be presented elsewhere.<sup>20</sup>

#### **II. EXPERIMENTAL DETAILS**

The crossed beam apparatus has been described in full detail elsewhere.<sup>21</sup> The necessary modifications for LIF studies under beam plus gas conditions are described in Fig. 1. A well collimated beam of ytterbium emanating from a differentially pumped source chamber traverses a tenuous halomethane gas inside the scattering chamber. The ytterbium metal, with a stated purity of 99.99% (Alpha-Ventron Corp.), is contained in a resistively heated stainless steel oven operated at 480 °C, corresponding to a vapor pressure of  $\gtrsim 10^{-2}$  Torr.<sup>22,23</sup> The halomethane gas is introduced into the scattering center through a coarse glass frit (area  $\approx 1$  cm<sup>2</sup>). The

reactants attempted include  $CH_2Cl_2$ ,  $CHCl_3$ ,  $CCl_4$ ,  $CF_3Cl$ ,  $CH_3Br$ ,  $CH_2Br_2$ ,  $CHBr_3$ ,  $CBr_4$ ,  $CF_3Br$ ,  $CH_3I$ ,  $CH_2I_2$ ,  $CF_3I$ ,  $CF_2Cl_2$ , and  $CFCl_3$ . Some of these reagents, especially  $CH_3I$ ,  $CH_2I_2$ ,  $CH_2Br_2$ , and  $CHBr_3$ , have had to be vacuum distilled immediately prior to use.

The background pressure in the cryogenically pumped scattering chamber is typically  $< 10^{-7}$  Torr. The oxidizer gas pressures are maintained in most cases at much less than  $2 \times 10^{-4}$  Torr during the runs to ensure "single-collision" conditions. However, the actual pressures in the scattering center may be substantially higher, since the measuring ionization gauge is located 100 cm away. Nevertheless, vibrational quenching is known to be negligible at pressures  $\leq 10^{-3}$  Torr, <sup>24</sup> and thus would not affect the conclusions reached in this report.

The unrelaxed YbX products are excited directly in the scattering region by a continuous wave (cw) tunable dye laser (Spectra-Physics model 375) pumped by a 3 W multimode  $Ar^*$  laser. Typical dye laser power ranges from 10 to 300 mW. Scattered laser light is minimized by the usual array of baffles. The dye laser contains a three-layer Lyot filter within its cavity and has a measured bandwidth (FWHM) of 0.27 Å near 5550 Å. The dyes used, rhodamine 6G and 110, span the region 5350-6450 Å. Wavelength tuning is achieved by rotating the Lyot filter with a stepping motor. In many instances the wavelength scale is found not to be linear. Thus, a number of runs were made with trace amounts of Ba and Sm to generate line spectra for calibration purposes.

The laser-induced fluorescence is collected by an f/1.5 lens and routed out of the scattering chamber through a 1.5 m glass optical fiber. The signal is sensed by a cooled (-30 °C) photomultiplier tube (RCA C31034) operated at 1650 V to yield an optimized pulse height distribution. To permit phase-sensitive detection the signal is modulated by chopping the laser light or, in some cases, the oxidizer gas beam (at~65 Hz) and photon counted.

#### **III. RESULTS**

Figures 2-5 show some excitation spectra representative of each of the four YbX products. (In the reac-

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tions of Yb with  $CH_2Cl_2$  and  $CF_3Cl$ , no products could be detected. On the other hand, it appears that the reaction Yb + CHCl\_3 does proceed, but must be undertaken at pressures exceeding  $5 \times 10^{-4}$  Torr; hence, the results were discarded.) Each vibrational band in the LIF spectra could be confidently assigned to the YbX ( $A^2\Pi_{1/2}$ -



FIG. 2. YbF excitation spectrum from the reaction  $Yb + CF_2Cl_2$ . Band heads are labeled according to Ref. 16.

 $X^{2}\Sigma^{*}$ ) band system. To be sure, the formation of triatomic products, such as  $CX_{2}$ , CHX, and  $CH_{2}$ , are energetically allowed and some of these species possess absorption bands within the excitation region. However, the absence of any bands not attributable to YbX suggests that a dominant channel in these reactions is the formation of YbX.<sup>25</sup> Extensive vibrational analyses of the band heads are published elsewhere.<sup>20</sup> Table I summarizes the reactions included in this study, together with the highest populated v'' extrapolated in each case and the values for the other relevant parameters.

In the Yb + RX systems the fraction of total reaction energy channelled into the YbX products could, in principle, be derived from the YbX excitation spectra. Nor-



FIG. 3. YbCl excitation spectrum (using rhodamine 110 dye) from the reaction  $\rm Yb+CCl_4.$ 



FIG. 4. YbBr excitation spectrum (using rhodamine 110 dye) from the reaction  $Yb + CH_2Br$ .

mally, trial sets of vibrational and rotational distributions are convoluted with the measured laser bandwidth profile until satisfactory matching with the experimental LIF spectra is attained. Unfortunately, rotational constants for YbCl, YbBr, and YbI are not available; and, although satisfactorily accurate constants for YbF have been derived, the presence of extensive and uncharacterized perturbations at J > 25 severely restricts the reliability of any computer-synthesized spectra. Furthermore, the primary data from the LIF spectra are product number densities. Thus, even if the necessary spectroscopic constants were available, one would still require the average product velocity for each v level in order to compute the vibrational state populations. For these reasons the application of reasonable approximations becomes inevitable.

In the analysis of the LIF spectra of the alkaline-earth monohalides, 4,7 the assumption of constant Franck-Condon factors (FCF) within the  $\Delta v = 0$  sequence has become customary. This is justified by the fact that the FCF's for transitions between the low v levels are heavily biased in favor of this sequence. Such an approximation, however, cannot be simply extended to the ytterbium monohalide systems. The analyses  $^{16-18,20}$  of the YbX spectra show that the potential energy curves for the Aand X states are not entirely harmonic. Furthermore, at least in the case of YbF the equilibrium internuclear distance of the ground state potential curve differs significantly from those of the low-lying electronically excited states. As a result, there exists a rapid decline in the FCF's with increasing v within the  $\Delta v = 0$  sequence. Furthermore, the FCF's actually "oscillate" in magnitude, as indicated by the disparate structure of the satellite ( $\Delta v \neq 0$ ) sequences.

The preceding comments suggest that all the sequences observed within the A-X band system must be employed to obtain sufficiently accurate vibrational state populations.<sup>26</sup> The intensity of each (v', v'') band is proportional to several parameters

$$I(v', v'') \sim N_{v''} q_{v', v''} \rho_{v', v''} , \qquad (1)$$

where q and  $\rho$  represent the Franck-Condon factor and laser intensity, respectively. Since we are only interested in the relative vibrational state populations, we

TABLE I. Summary of reactions studied (energy units in kcal/mol).<sup>a</sup>

Reactant	Product	$v_{\max}^{\prime\prime}$	E	$\langle E_{v''} \rangle$	Ei	$D_0^\circ$ (RX)	$D_0^\circ$ (YbX)
CCl <sub>2</sub> F-F	YbF	3	4.3		3.3	$113 \pm 2$	$114 \pm 2$
$CFCI_2 - CI$	YbC1	22	17.0	11.9	3.7	$73 \pm 3$	$86 \pm 3$
CCl <sub>3</sub> -Cl	YbC1	27	20.6	16.3	4.0	$70 \pm 3$	$86 \pm 3$
CH <sub>3</sub> -Br	YbBr	11	6.1	1.6	2.2	$68 \pm 2$	$72 \pm 2$
CF <sub>3</sub> Br-Br	YbBr	18	9.8	5.8	2.1	$61 \pm 3$	$69 \pm 3$
CH <sub>3</sub> -Br	YbBr	18	9.8	5.5	3.0	$68 \pm 3$	$75 \pm 3$
С Н <sub>3</sub> -І	YbI	11	4.6	1.4	1.5	$55 \pm 2$	$58 \pm 2$
CH <sub>2</sub> I-I	YbI	16	6.7	3.5	2.6	$51 \pm 2$	$55 \pm 2$
$CF_3 - I$	YbI	18	7.5	5.1	2.1	$53 \pm 1$	$58 \pm 1$

 ${}^{a}v'_{max}$  = highest v level of YbX product extrapolated from the LIF spectra (cf. Fig. 6);  $E_{v'_{max}} = G(v'_{max}) - G(0)$ ;  $\langle E_{v''} \rangle$  = average energy appearing as YbX vibration;  $E^{i} = \text{total reactant energy}$  $= E_{\text{trans}}^{i} + E_{\text{rot}}^{i} (RX) + E_{\text{vib}}^{i} (RX)$ ;  $D_{0}^{\circ} (RX)$  = dissociation energies, computed using the thermochemical data of Ref. 63;  $D_{0}^{\circ} (YbX)$ = lower bounds for YbX dissociation energies.

can obtain the ratio  $N_{v_2'}/N_{v_1'}$  by summing up the band intensities originating from v'' over all final states v':

$$\frac{N_{v'_{2}}}{N_{v'_{1}}} \approx \frac{\sum_{v'} I(v', v'_{2})}{\sum_{v'} I(v', v'_{1})} .$$
(2)

In applying Eq. (2) the LIF spectra have been normalized to constant laser intensity. For simplicity, band head peaks are used and corrections are made in regions where serious overlapping of sequences occurs. The relative populations are subsequently normalized to unity. The results are depicted in Fig. 6, with the exception of three reactions. In the case of Yb+CHBr<sub>3</sub>, CBr<sub>4</sub>, very high vibrational levels of YbBr are populated and extensive merging of sequences has precluded any useful analysis of the YbBr spectra. In the case of Yb+CCl<sub>2</sub>F<sub>2</sub>, on the other hand, only four vibrational levels within the  $\Delta v = 0$  sequence in YbF could be detected. Thus, no attempt has been made to estimate the relative vibrational state populations of the YbF products.

Although the highest v'' levels detected in the YbX products actually fall considerably below the energetic limits, the experimental data available (indicated by solid lines) clearly depict a bell-shaped distribution in each case. The relative populations in other v'' levels



FIG. 5. YbI excitation spectrum (using rhodamine 6G dye) from the reaction  $Yb + CH_3I$ .



FIG. 6. Plots of the relative vibrational distributions P(v'') as a function of the vibrational level v''.

are then extrapolated from the general shape of these distributions. The results closely resemble those of the alkaline-earth analogs and indicate that in these M + RX systems the reaction energy is not statistically distributed among the available vibrational levels of the MX products.

At least two factors restrict the accuracy of the results shown in Fig. 6. As mentioned previously, we have disregarded the variation of YbX product velocities with v'' and assumed that the distributions based on product number densities closely match those based on flux densities.<sup>27</sup> Secondly, in some cases the laser excitation between 5400 and 6400<sup>-Å</sup> does not cover more than 70% of the entire A-X band system. These limitations are not expected to significantly distort the bellshape features in Fig. 6, but will likely shift the positior of the peaks in the vibrational distributions.<sup>26</sup> Despite these limitations, the results in Fig. 6 enable us to extract qualitative features in the reaction dynamics.

The fraction  $\langle f_{Y} \rangle$  of the total reaction energy  $E_{\rm tot}$  released into YbX product vibration is crudely estimated from

$$\langle f_{v} \rangle = \langle E_{v'}, \rangle / E_{tot}$$
,

where

$$\langle E_{v^{\prime\prime}}\rangle = \sum_{v^{\prime\prime}} E_{v^{\prime\prime}} P(v^{\prime\prime}) / \sum_{v^{\prime\prime}} P(v^{\prime\prime}) \ . \label{eq:eq:expansion}$$

Here  $E_{v''}$  is the energy of the rotationless vibrational level v''. The results are summarized in Table II, along with published data from analogous reactions involving the alkaline earth metal atoms.<sup>7-9,28</sup> Despite the crude approximations employed, the trends in  $\langle f_v \rangle$ in the Yb + RX reactions are found to parallel those in the alkaline-earth analogs.

#### IV. DISCUSSION

The electron-jump model, 29,30 which has been fairly successful in correlating gross features in the dynamics of alkali atom plus halogen systems, provides a convenient starting point for our discussion. A straightforward analysis will show that this simple model could be extended to the Yb + RX systems.<sup>31</sup> Ytterbium has the electronic configuration [Xe]  $4f^{14} 6s^2$  in its ground state. The first electron jump involves the transfer of one valence electron of Yb into the lowest unoccupied molecular orbital (LUMO) of RX. This process occurs in the vicinity at which the covalent Yb + RX and ionic  $Yb^{+} + RX^{-}$ potential energy surfaces intersect, determined by  $r_e = e^2/\Delta$ , where  $\Delta$  is the difference between the ionization potential of Yb (6.2 eV) and the electron affinity of RX. Unlike the alkali atom systems, however, a second electron jump might well occur in reactions involving Yb atoms. Such an event, if it takes place in the entrance channel, necessitates the removal of the second 6s electron of Yb. Ionization of Yb<sup>+</sup>, however, requires 12.2 eV.<sup>34</sup> Thus, almost regardless of the magnitudes of RX<sup>-</sup> electron affinities, <sup>35</sup> energetics may force the second electron transfer to occur, instead, as the products separate. This process involves a transition between the YbX + R and  $YbX^{+} + R^{-}$  potential energy surfaces and would be more likely because the ionization potentials of YbX are approximately equal to that of Yb.<sup>19</sup> Indeed, this mechanism may well account for the obser-

TABLE II. Fraction of reaction energy released into MX product vibration (in percent).

X X	CF3X	сн <sub>з</sub> х	CH <sub>2</sub> X <sub>2</sub>	снх <sub>з</sub>	CX4				
СІ	NP	NP	NP	SNA	81				
	NP	NR	NR	68	75				
Br	55.8	17.4	36.5	SNA	SNA				
	(88)	(28)	(52)	(85)	(96)				
I	68.4	30.4	34	NA	NA				
	>75	44	62	NR	NR				
- This work NA - not attempted									
$\overline{\bigcirc}$	8a + RX		NP	NP - no products detected					
$\bigcirc$			SNA	SNA — spectrum not analyzed					
( F	orted								

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(3)

vation of considerably large chemi-ionization cross sections in the M + XY reactions<sup>19</sup> and may eventually reconcile any significant difference in the reactive behavior of the alkali and alkaline-earth atoms.

The picture outlined above, however simplistic, suggests that Yb, alkali, and alkaline earth plus RX systems might exhibit similar reactive patterns.  $^{36,37}$  Thus, the semiquantitative data on the energy disposal in the Yb+RX systems, summarized in Table II, may be more conveniently evaluated in the light of the results from the well-studied alkali and alkaline earth counterparts. To this end we adopt the impulsive, "photodissociation" model due to Herschbach<sup>40</sup> and Harris<sup>41</sup> to correlate qualitatively the observed trends in energy disposal.

Several trends are obvious from Table II. First of all, one notes that more energy is released into YbX product vibration in the Yb +  $CH_2X_2$  systems compared with the Yb +  $CH_3X$  systems; this correlates with the results from unimolecular photofragmentation spectroscopy of  $CH_3I^{42}$  and  $CH_2I_2$ , <sup>48</sup> where 84% and 10%-20%, respectively, of the total energy are found to be deposited into product recoil. This trend has previously been observed from studies of the alkali systems. For instance, while in the K +  $CH_3I$  reaction, <sup>49</sup> a substantial fraction (~60%) of the reaction energy is channeled into product recoil, primitive angular scattering data<sup>50,51</sup> of K and Cs +  $CH_2I_2$  suggest that roughly 10% of the reaction energy is released into product translation.

The trend across the rows in Table II also follows the degree of forward peaking observed in the scattering of alkali iodides from the  $M + CH_3I$ ,  $CH_2I_2$ , and  $CHI_3$  reac-



FIG. 7. Comparison of the YbBr and YbI product vibrational distributions from three groups of Yb + RX reactions. The data are recast from Fig. 6 into  $P(f_v)$  vs  $f_v$ .

tions.<sup>50-52</sup> The increasing tendency for a "stripping" mechanism is reflected in a greater release of reaction energy into the newly formed MI bond. As Lin et al.<sup>52</sup> have pointed out, this trend in the alkali atom plus RX dynamics is in accord with the observed corresponding trends<sup>53</sup> for dissociative electron attachment in RX. It appears that the electron affinity increases while the repulsive energy along the C-X bond upon electron attachment decreases with the number of X atoms in RX. This leads one to suspect that the dynamics might be more sensitive to the degree of halogenation in RX than to the nature of X, and that more detailed dynamical features may be revealed from a comparison of the patterns in the vibrational, rotational, and/or translational distributions. One approach would be to group the plots of Fig. 6 and recast them as a function of  $f_v$ , the fraction of  $E_{tot}$  in vibration. The results of such a plot are illustrated in Fig. 7. One notes that, although the total number of vibrational levels populated differ for YbBr and YbI within each group of Yb + RX reactions, the profiles of the distributions reveal a marked resemblance. Our data are by no means quantitative, as already emphasized, but it may well be that quantitative data of vibrational state population rates plotted in this manner will depict a much more perfect resemblance.

Even more dramatic than Fig. 7 is a comparison of the MX product vibrational distributions from the reactions of RX with different metal M atoms. If the role played by the LUMO of RX is of prime importance, one would expect the dynamics of M + RX reactions to exhibit similar patterns for all metal atoms of comparable ionization potentials. In Fig. 8 we have recast the YbCl distribution (from the Yb + CCl<sub>4</sub> reaction) as a function of  $f_v$  in order to compare it with more quantitative results from the analogous Ba, Ca + CCl<sub>4</sub> reactions.<sup>8,54</sup> The resemblance is again apparent.

The preceding paragraphs reflect our optimistic belief that one or more parameters may eventually be found



FIG. 8. Plots of the relative vibrational distributions  $P(f_v)$  as a function of  $f_v$ , the fraction of  $E_{tot}$  in vibration, for the MCl products from the reactions of CCl<sub>4</sub> with Yb, Ba, and Ca. The results from the Ca, Ba+CCl<sub>4</sub> reactions have previously been plotted as a function of  $v/v_{max}$  (Ref. 54).

that could unify all the dynamical features in these M + RX reactions (and perhaps even in the M + HX systems). It is, however, a moot question whether that parameter would be  $f_V$ ,  $f_R$ , or  $f_T$ . In a detailed analysis of the K, Ba + CH<sub>3</sub>I and CF<sub>3</sub>I reactions, Bernstein and Wilcomb<sup>55</sup> have found that the unifying variable is the product recoil momentum, and not  $E_{vib}$  or  $f_V$ . Levine and co-workers<sup>56</sup> have used another impulsive model incorporated into the framework of the information-theoretic approach to correlate some of the essential features of these reactions. Further discussion must be postponed until more quantitative data, notably on differential state-to-state cross sections, become available.

Our remarks thus far have been confined to those reactions of a metal atom M with unmixed halomethanes. It is reasonable to assume that the initial stage of the reactions with those RX containing more than one type of halogen is likewise governed by an electron jump. In this case the valence electron enters an antibonding orbital of RX that is located primarily near the least electronegative (at the same time the heaviest) halogen. Thus, in the reactions  $M + CF_3X$  (X = Cl, Br, I) the dominant salt product is expected to be MX even though the channel leading to the MF product is in some cases the more excergic. In other words, the primary "macroscopic" branching yields MX. Numerous supporting evidence has been cited, including the reactive systems of Na, 57, 58 K, 59 and the alkaline earth atoms. 44, 52 The reactions of Yb with CF<sub>3</sub>Br and CF<sub>3</sub>I prove to be no exception, although, fortuitously, the pathway yielding the YbF product is probably endoergic. Similar arguments predict the main salt product of an  $M + CFCl_3$  reaction to be MCl. This is again supported by our present study and by recent data on Ba + CFCl<sub>3</sub>.<sup>28</sup> An apparent exception appears to be the  $Yb + CF_2Cl_2$  system. In this case the only product detected is YbF, although the YbCl product is also energetically possible. The signal is, however, extremely weak; a rough estimate indicates that the reaction cross section is smaller than that of Yb+CFCl<sub>3</sub> by at least a factor of 20. To reconcile these findings, we are tempted to speculate that the dissociation asymptote for  $CFCl_2 + F$  lies below that for CF<sub>2</sub>Cl + Cl<sup>-</sup>.<sup>60</sup> Moreover, an activation barrier may be present along the channel leading to the YbCl product. This could explain why the MCl product has not been detected in numerous other exothermic reactions, including Yb + CF<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub> and Ba + CF<sub>3</sub>Cl, CH<sub>3</sub>Cl.<sup>28,61</sup> The determination of the heights of these activation barriers may prove to be a fruitful ground for future experiments employing accelerated beams and stateprepared reactants.

The observed trend in the dissociative electron attachment in RX also predicts the relative extent of internal excitation in the MX product. Since the  $CX_nY_{4-n}$ molecules have substantially larger electronegativities than  $CH_nX_{4-n}$ , the systems  $M + CX_nY_{4-n}$  are expected to yield larger reaction cross sections, with a correspondingly higher fraction of  $E_{tot}$  released into the internal excitation of the salt product. This is amply substantiated by the results summarized in Table II, as well as other data from the Ba,  $Sr + CH_3Br$ ,  $CF_3Br$ ,  $CH_3I$ ,  $CF_3I^{28}$ 

#### and $K + CH_3I$ , $CF_3I^{55}$ reactions.

In conclusion, we stress once again that our present studies suggest a very striking resemblance between the characteristics of Yb plus halomethane reactions and those of the analogous alkaline-earth systems. Such a close similarity has also been found to exist in the analogous Sn and U reactions.<sup>31+33,62</sup> It is thus pleasing to find that general conclusions drawn from the studies of the alkali and alkaline-earth atom reaction dynamics can be generalized to a large class of systems involving other metal atoms.

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