| | |
|---|---|
| 2 Cl Thiophene | 6.65 |
| $2CH_3$ Thiophene | 17.32 |

These data correlate well with the ionization potentials calculated for the quenchers from charge transfer complexes studies previously done, and therefore a mechanism involving a charge transfer complex formed between the excited butyrophenone in its triplet state and the quencher is postulated. According to the mechanism the energy content of the triplet states of the thiophenic compounds used in this work should be greater than 74.1 kcal/mole which is the energy content of the $^3$Bu.

### δ3

## Photoionization Processes at Threshold: Direct and Auto-Ionization and Franck-Condon Factors for Simple Molecules

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A threshold photoelectron-coincident photoion spectrometer has been constructed using a collimated hole structure for selection of near-thermal electrons. Calibration with rare gases demonstrated a resolution of 0.014 ev FWHM. Location of maxima is possible within less than 0.005 ev. Threshold photoelectron spectra lead directly to transition probabilities at threshold for direct processes, without concern for variation in the ionization cross section past onset. Contributions from intense autoionizing states just above the onset of direct processes introduce a complication resulting from incomplete rejection. Preionization can be identified by relative abundance measurements of threshold photoelectrons and photoions, or by reducing the resolution of the threshold detector by increasing the extraction field in the ionization region. Vibrational structure between the first and second electronic states of the ions is difficult to assess quantitatively because of such interferences; these become less important for higher electronic states. Comparison of our results with data obtained by other methods is made for the rare gases, nitrogen and carbon dioxide, and measurements on $BF_3$, $SF_6$, and other small inorganic fluorides will be summarized.

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### δ4

## Photoionization Mass Spectrometry of Alcohols, Alcohol Clusters and Carbon Dioxide Dimers

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Photoionization of hydrogen bonded alcohol clusters and clusters of carbon dioxide has been studied using a supersonic molecular beam sampling system, wavelength dispersed vacuum ultraviolet radiation produced from an electron storage ring, and a quadrupole mass spectrometer ion detector. In addition to a regular spectrum, the observed *m/e* intensities for methanol and ethanol samples display ions corresponding to the series $(ROH)_nH^+$, where $1 \leqslant n \leqslant 5$. From mixtures of methanol and ethanol, a complete series of mixed clusters $H^+(CH_3OH)_n(CH_3CH_2OH)_{4-n}$ $0 \leqslant n \leqslant 4$, was observed. Experiments performed to elucidate how and where these clusters are formed indicate that neutral cluster species are present in the sample gas in the molecular beam source chamber at pressures above 10 Torr, and that equilibrium conditions may exist above 35 Torr at 20 °C. Photoionization efficiency curves for the methanol cluster species show appearance potentials in the order *m/e* 129(9.3 eV) < 97(9.5 eV) < 65(9.8 eV) < 33(10.2 eV) < 32(10.84 eV). This ordering, as well as high observed cluster ion intensities and low equivalent pressures in the ion source, leads us to exclude ion–molecule reactions as the major source of the detected ions.

If an equilibrium process is assumed for the neutral cluster and each cluster produces a unique ion, the relative intensities of the cluster ions as a function of molecular beam source gas temperature can produce thermochemical information on the following neutral cluster equilibria:

$$(CH_3OH)_n \rightleftarrows (CH_3OH)_{n-1} + CH_3OH \quad (1)$$

where the cluster association is assumed to arise from hydrogen bonding. Linear van 't Hoff type plots are obtained for methanol in the temperature region near the condensation point. Preliminary measured ΔH values for each member in the series of reaction (1) at 100 Torr are as follows: ($n$, $n-1$ in parenthesis): (2,1) 4.6 kcal/mole; (3,2) 2.0 kcal/mole; (4,3) 1.1 kcal/mole, and (5,4) 0.4 kcal/mole. These values must remain tentative until the contribution from additional clustering in the beam expansion and other contributions to cluster intensity can be explored.

Cluster formation with carbon dioxide as sample gas appears to be dominated by growth in the molecular beam expansion jet. At very short nozzle-skimmer (NS) distances (of the order of 2 nozzle diameters), essentially no $CO_2$ dimer intensity is observed. Under relatively severe expansion conditions (320 Torr $CO_2$ pressure, —40 °C nozzle temperature, NS distance = 23 nozzle diameters) cluster ions corresponding to $(CO_2)_n^+$ with $1 \leqslant n \leqslant 20$ are observed, with the upper limit defined by our maximum mass spectrometer scan range. The photoionization efficiency curve of $CO_2$ dimer, *m/e* 88, taken under molecular beam conditions such that only the dimer is produced shows that the *onset* of ionization is shifted 0.37 eV lower than the onset of the molecular ion with substantial broadening of the autoionization structure in the spectrum. Only three broad autoionizing peaks in the 700 - 800 Å region of the *m/e* 88 photoionization efficiency curve were observed, and these peaks could be fit to a Rydberg series with a limit of 18.04 eV, slightly lower than the 18.07 eV energy of the $B^2\Sigma_u^+$ state in $CO_2^+$. These features may provide insight into the structure of the dimer. Finally, the photoionization efficiency curves of *m/e* 88 taken at higher photon energies than 14 eV and under molecular beam conditions which produce significant amounts of higher polymers shows strong evidence of higher cluster ion fragmentation enhancing the *m/e* 38 intensity.

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## Chemiluminescence from Alkyl Hyponitrite Decomposition

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Chemiluminescence was observed from solutions of dibenzyl hyponitrite and 2-pentyl hyponitrite at 25 - 70 °C. At 53.5 ± 0.3 °C in benzene, the rate constant for decay of chemiluminescence from dibenzyl hyponitrite below about 0.03 *M* was $(7.9 \pm 0.4) \times 10^{-4}\ s^{-1}$, alone and in the prescence of 0.00027, 0.0027, or 0.026 *M* 9,10-dibromoanthracene (DBA) as a luminescence enhancer. At higher concentrations of benzyl hyponitrite the decay occurred at an accelerated rate, which is presumably associated with an induced decomposition. [1] In carbon tetrachloride and with 0.026 *M* 9,10-dibromoanthracene, the initial light intensity from 0.010 *M* dibenzyl hyponitrite was about 2.5 fold greater than in benzene, although the same rate constant for decay was observed ($7.9 \times 10^{-4}\ s^{-1}$ at 53.3 °C).

The following kinetic scheme and equations were assumed:

$$\begin{array}{lcl}
B_zH & \xrightarrow{1} & 2\ PhCh_2O\cdot + N_2 \\
2PhCH_2O\cdot & \xrightarrow{2} & PhCH_2OH + PhCHO \\
 & \xrightarrow{3} & PhCH_2OH + PhCHO^1 \\
 & \xrightarrow{4} & PhCH_2OH + PhCHO^3 \\
PhCHO^1 & \xrightarrow{fast} & PhCHO^3 \\
PhCHO^3 & \xrightarrow{5} & PhCHO \\
PhCHO^3 + DBA & \xrightarrow{6} & DBA^1 + PhCHO \\
DBA^1 & \xrightarrow{7} & DBA + h\nu \\
DBA^1 & \xrightarrow{8} & DBA
\end{array}$$

$$I = \frac{dh\nu}{dt} = \frac{k_1k_6k_7\ [DBA]}{(k_6 + k_7)} \times \frac{(k_3 + k_4)}{(k_2 + k_3 + k_4)\ (k_5 + k_6\ (DBA))}\ [B_zH]$$

A plot of $I$ *vs.* $[B_zH]$ in the presence of 0.027 *M* DBA could be represented by a straight line that intersected the origin and data points up to 0.03 *M* in $B_zH$.

Our observations are consistent with, but do not demand the hypothesis that the very week chemiluminescence associated with auto-