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Photofragmentation of $(\text{CO}_2)_n^+$: Simple energy dependence for the number of neutrals ejected, $13 < n < 26^a$

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The photodissociation of small molecules in condensed media has been studied by many¹⁻⁹ workers over the past decade, where the "caging" mechanics of the nascent photo-products by nearby solvent molecules has been of primary interest. It has recently been proposed^{10,11} that these local structures can be more carefully studied by initiating photodissociation in a small cluster consisting of a controlled number of solvent molecules surrounding the chromophore. In this paper, we present the results of such a study of $(\text{CO}_2)_n^+$, where the cluster size is established by mass analysis and where visible photoexcitation has been shown^{12,13} to involve rupture of a dimer absorber into its monomeric components. The mass-analyzed photofragment ions yield insight into the unimolecular decay processes undergone by the energized parent. We find that $(\text{CO}_2)_n^+$ absorbers with $n > 13$ photodissociate with a constant neutral mass loss per unit photon energy.

The experimental apparatus has been previously¹³ described. Briefly, CO_2^+ ions are formed by crossing a supersonic expansion of pure CO_2 with an electron beam 2 mm below the nozzle. The monomer ions drift in the expansion, while the ionic clusters are synthesized via subsequent nucleation reactions. The ions are then pulse-ejected into a tandem TOF mass spectrometer, which provides both mass selection before photoabsorption and mass identification of all product photoions.

All clusters investigated were found to photodissociate in the region of the dimer¹⁴ absorption. The $(\text{CO}_2)_n^+$ photofragmentation pattern resulting from excitation at 1064 nm is shown in Fig. 1 for $n = 2$ to 26. The horizontal lines indicate the range of energetically allowed photofragments for each parent. The observed photofragment distributions, indicated by vertical lines, clearly occupy only a small fraction of this range. For all parents, and at all photon energies studied, the FWHM of the fragment distribution is less than two monomer units. Moreover, at high n the fragment masses have a constant displacement from the parents. Loss of a single moiety, the dominant fragmentation channel observed¹⁵⁻²⁰ in collision-induced dissociation, is not observed in this work.

While the width of the daughter ion distributions does not change with excitation wavelengths, the *mean* of the distribution, n_{av} , depends strongly upon the photon energy. It is useful to characterize these distributions by the parameter m , the average number of CO_2 neutrals ejected, where

$$m = n_p - n_{av}$$

and n_p is the parent cluster size. This quantity is plotted in Fig. 2(a) for $n_p = 2-26$ at excitation wavelengths 1064, 650, and 532 nm. At each wavelength, m smoothly increases with parent cluster size, and approaches a constant value dependent on the photon energy. The constant displacement of daughter ions from parents observed in Fig. 1 results from a constant loss of six neutral CO_2 molecules [see Fig. 2(a)] for parent cluster size > 13 .

Figure 2(b) presents a plot of the asymptotic value of m as a function of photon energy. It is striking that the number of neutral CO_2 molecules ejected is approximately proportional to the excitation energy. In the very likely event that photodissociation of the higher clusters proceeds via sequential loss of neutral CO_2 monomers, the slope of the line gives an upper bound of 4.9 kcal/mol for the CO_2 -cluster bond energy. This value is close to, but *less than*, the energy of

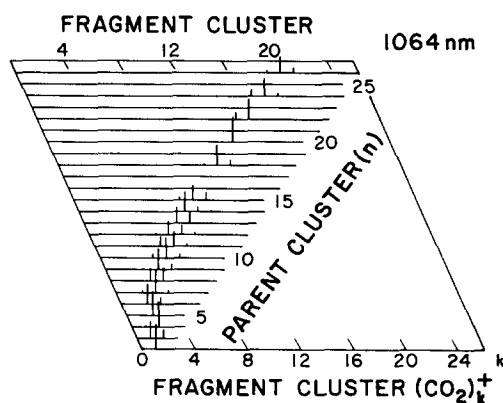


FIG. 1. Photofragmentation patterns for $(\text{CO}_2)_n^+$ ions, $n = 2-26$, resulting from excitation at 1064 nm. The parent cluster size is shown on the depth axis, and the product ion cluster size on the x axis. The height of each stick indicates the relative intensity of products from a given absorber.

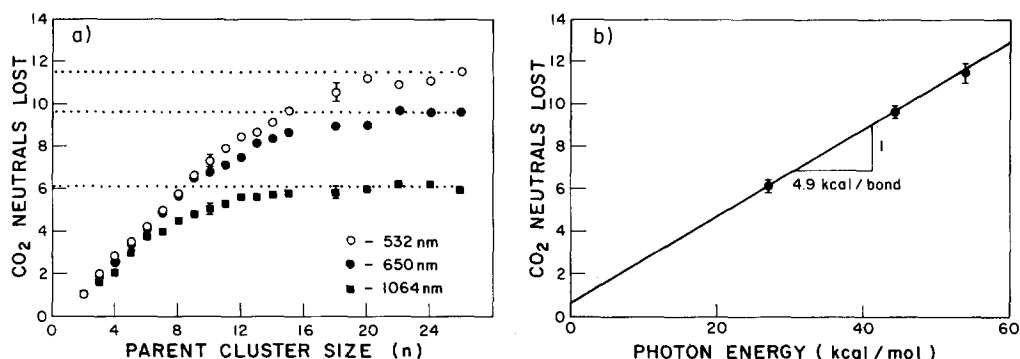


FIG. 2. (a) The average number of neutral CO_2 molecules ejected from a given cluster as a function of absorber size. Data are obtained at 1064, 650, and 532 nm, corresponding to the low-, mid-, and high-energy portions of the dimer cation charge-transfer absorption band. (b) The asymptotic number of CO_2 molecules lost [dotted lines in (a)] as a function of photon energy. The slope gives an upper bound of 4.9 kcal/mol for the bond energy.

sublimation for bulk CO_2 , 5.7 kcal/mol. Thus the outer shell of these ionic clusters indeed appears to be governed by forces similar to those present in bulk CO_2 .²¹ Note that a linear dependence of the number of asymptotic bonds broken vs photon energy [Fig. 2(b)] implies that the binding energy is nearly constant over the cluster range from $(n_p - m)$ to n_p . From Fig. 2(a), this condition appears to be satisfied for $(n_p - m) > 13$.

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NOTES

The contribution of intramolecular vibrations to the observed structure of liquid water

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Recently, we reported^{1,2} the results of path integral Monte Carlo studies using the ST2³ model of water. These studies determined the magnitude of the effect of quantization of intermolecular degrees of freedom on both the structure of liquid water and the structural differences between light and heavy water. In this note, we consider an approximate treatment of intramolecular effects (zero point vibrations) for the atom-atom radial distribution functions (RDF) and the related partial structure factors.

Stillinger⁴ has described formally the effects of internal

molecular vibrations on the distribution of relative intermolecular coordinates, and the corresponding prescription for a (vibrationally averaged) rigid body intermolecular potential. Accordingly, results from rigid body simulations using empirical potentials can be viewed as providing approximate predictions for the correct intermolecular coordinate distribution. The influence of intramolecular vibrations can then be superimposed on these results, to a first approximation, to estimate the effects of interest here.

The approximation we use is to replace the ST2 geome-