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Photodissociation of CO_3^- ·H₂O: Observation of the O^- ·H₂O + CO_2 product channel

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A new product channel, $O^- \cdot H_2 O + CO_2$ was discovered in the photodissociation of $CO_3^- \cdot H_2 O$. Experiments were conducted by crossing a mass selected 8 kV ion beam with a. linearly polarized laser beam and measuring the kinetic energy distributions of the charged photodissociation products. Distributions were collected at photon energies of 2.41, 2.54, and 2.71 eV. By varying the angle between the ion and the laser polarization vector, product angular distributions were obtained. Relative photodissociation cross sections of this process were determined by comparisons with known processes: a) $CO_3^- \cdot H_2 O + h\nu \rightarrow CO_3^- + H_2 O$ and b) $CO_3^- + h\nu \rightarrow O^- + CO_2$. Ab initio calculations focusing on geometric structure and vibrational frequencies of the ground state of $O^- \cdot H_2 O$ were performed using GAUSSIAN 82 and GAUSSIAN 88 programs. With both MP2/6-31G** and MP2/6-31 + G* basis sets, the lowest energy structure obtained constants obtained from these calculations were employed in statistical phase space modeling. Phase space theory indicated a photoinduced "intracluster" reaction mechanism was responsible for this novel product channel.

I. INTRODUCTION

The importance of molecular negative ions and ionic clusters in ionospheric chemistry has prompted numerous laboratory studies over the past decade. Besides providing chemical and physical data necessary for atmospheric modeling, these studies also report on the thermochemistry, kinetics, and spectroscopy of various species. Work done on the CO_3^- ion and its weakly bound clusters is a case in point. CO_3^- is believed to be a dominant ion in the mesosphere and is found throughout other regions of the earth's atmosphere.¹⁻³ Hydrates of CO_3^- have also been detected and are found to exhibit similar photophysical characteristics to CO_3^- .⁴⁻¹⁰

Photodissociation experiments have proven valuable in the study of such weakly bound negative ions and ionic clusters. The identity of the photofragments following laser excitation and the partitioning of the photon energy among the various degrees of freedom of the photofragments are of particular interest. It has been known for some time that $CO_3^- \cdot H_2O$ photodissociates at visible wavelengths to yield $CO_3^- + H_2O$ as products.⁴⁻¹⁰ Results of our photodissociation study on $CO_3^- \cdot H_2O$ forming CO_3^- and H_2O were reported in detail in a previous paper⁴ and will only be briefly reviewed here. The important asymptotic energies for the system are given in Fig. 1. The proposed mechanism for photodissociation of $CO_3^- \cdot H_2O$ into CO_3^- and H_2O is the following: (1) Photon absorption occurs via transition localized on the CO_3^- chromophore; (2) The excited state internally converts to the $CO_3^- \cdot H_2O$ ground state, with a high degree of vibrational excitation localized on the $CO_3^$ moiety; (3) The vibrational excitation localized on the $CO_3^$ moiety begins to slowly randomize throughout the cluster ion; (4) Before complete energy randomization has occurred, $CO_3^- \cdot H_2O$ dissociates to CO_3^- and H_2O . Only a small fraction of the available energy is partitioned into translation of the nascent CO_3^- , leaving CO_3^- with a significant amount of internal energy. Small kinetic energy releases in the dissociation, as well as isotropic product angular distributions, support the idea that the photoexcited cluster leading to photodissociation is bound and long lived.

Previous work^{5,11-13} suggested that O⁻·H₂O/CO₂ might be a product channel in the photodissociation of $CO_3^- \cdot H_2O$. In this paper, we give experimental evidence that $O^- \cdot H_2 O/CO_2$ is indeed a product channel in the photo dissociation of CO_3^- ·H₂O and its kinetic energy distribution, angular distribution, and cross section (relative to CO_3^-) are determined. Ab initio molecular orbital calculations focusing on the geometric structure, cluster energies, and vibrational frequencies of the ground state of $O^- \cdot H_2 O$ are performed using the GAUSSIAN 82 and GAUSSIAN 88 set of programs and results are reported. Phase space theory implementing the theoretical parameters is used to model the observed product kinetic energy release distributions. Different isomeric parent and product ions are considered by comparing experimental and statistical phase space modeled kinetic energy distributions in an effort to understand the mechanism of this interesting reaction.

II. EXPERIMENTAL

The experimental method has been described in detail elsewhere^{14,15} and will only be briefly reviewed here. Figure

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FIG. 1. Schematic diagram showing energy states of importance in this work.

2 shows a schematic of the apparatus. The $CO_3^- \cdot H_2O$ ion was produced in a high pressure temperature variable ion source containing pure CO_2 . No additional H_2O was added as residual H_2O impurities in the CO_2 feed gas and gas inlet system proved adequate. The likely mechanism for cluster ion formation is:

$$CO_2 + e^- \rightarrow O^- + CO,$$

$$O^- + CO_2 + M \rightarrow CO_3^- + M$$

$$CO_3^- + H_2O + M \rightarrow CO_3^- \cdot H_2O + M$$

where M is a bath gas molecule (CO₂ in the present work). The CO₂ pressure in the ion source was ~0.25 Torr and the ion source temperature was held at ~273 K. Ions that effused out of the source were accelerated to 8 kV, mass selected by the magnet, and brought to a spatial focus where they were crossed by light from an argon ion laser. Photon energies of 2.41, 2.54, and 2.71 eV were employed. A polarization rotator was used to vary the angle between the electric vector of the laser beam and the ion beam direction. Angles of 0°, 54.7°, and 90° were used. Photofragment ions were mass and energy analyzed by a high resolution electrostatic analyzer and detected using single ion counting. Background signals, due to metastable reactions or collision induced dissociation (CID) processes, were subtracted by chopping the laser beam and doing up/down counting.

III. RESULTS

A. Photodissociation cross section

The apparatus used in the experiments reported here is not designed to measure absolute cross sections. However, the photodissociation cross section of $CO_3^- \cdot H_2O$ $+ h\nu \rightarrow O^- \cdot H_2O + CO_2$ could be determined relative to the $CO_3^- + h\nu \rightarrow O^- + CO_2$ process since $CO_3^- \cdot H_2O$ and $CO_3^$ coexist simultaneously under our experimental conditions. Thus, by comparing the photodissociation signals of each process at various wavelengths, relative cross sections were obtained. The relative intensity of the competing $CO_3^- \cdot H_2O + h\nu \rightarrow CO_3^- + H_2O$ channel was also measured and a branching ratio between the two channels was determined. Comparisons of these three processes were conducted at two wavelengths by normalizing their ion intensities.



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The results are given in Table I. The magnitude of the $CO_3^- \cdot H_2O + h\nu \rightarrow O^- \cdot H_2O + CO_2$ photodissociation cross section was found to be only a factor of 2 to 4 less than that of CO_3^- at both wavelengths, but is substantially less than the $CO_3^- \cdot H_2O + h\nu \rightarrow CO_3^- + H_2O$ channel. For example, at 514 nm, the photodissociation cross section of the CO_3^-/H_2O product channel is 31 times greater than the $O^- \cdot H_2O/CO_2$ product channel.

As noted in Table I, we measure a cross section for photo dissociation of CO_3^- ·H₂ O that is ~4 times that of CO_3^- at 2.41 eV photon energy and ~ 2.6 times that of CO₃⁻ at 2.54 eV photon energy. Both of these differences are in reasonable agreement with the earlier measurements of Smith et al.⁹ who report the $CO_3^- \cdot H_2O$ cross section is 4.5 ± 1.5 times larger than CO_3^- in this photon energy range. Our reported absolute cross section for $CO_3^- \cdot H_2O$ of $\sim 1 \times 10^{-18}$ cm³ is about a factor of 2.5 smaller than reported by Smith et al.,9 possibly because we normalize to the CO₃⁻ photodestruction cross section of Hiller and Vestal.¹⁶ It is very unlikely that the photoexcited CO_3^- or $CO_3^- \cdot H_2O$ survive from the photon absorption point to our detector (\sim several μ s flight time) and thus resulting in our smaller numbers. Phase space theory calculations⁴ indicate photoexcited $CO_3^- \cdot H_2O_3$ has a lifetime in the 10^{-8} to 10^{-9} s range.

B. Product kinetic energy distribution

Product kinetic energy distributions were obtained with the laser polarization at the "magic angle" of 54.7°. Using this configuration, the measured peak shape is independent of the product angular distribution.¹⁴ The kinetic energy distribution is obtained from the peak shape by simple differentiation followed by transformation from the laboratory to center-of-mass frame.¹⁷

Figure 3(a) shows the laboratory frame kinetic energy distribution of $O^- \cdot H_2 O$ from $CO_3^- \cdot H_2 O$ at a wavelength of 514 nm (2.41 eV). The resulting product kinetic energy distribution, in the center-of-mass frame, is shown in Fig. 3(b). The product kinetic energy distribution peaks near zero and falls off smoothly and essentially exponentially at higher product kinetic energies. Similarly shaped distributions were obtained at other wavelengths.

The average kinetic energy release values, \overline{E}_{t} , determined from the measured distributions, are reported in Table II. The energy available to the dissociating photoproducts, E_{av} , is given by

TABLE I. Relative cross sections

Process	$\lambda = 2.41 \text{ eV}$ Cross section (cm ²)	$\lambda = 2.54 \text{ eV}$ Cross section (cm ²)
$\frac{1}{\operatorname{CO}_{2}^{-} + h\nu \rightarrow \mathrm{O}^{-} + \mathrm{CO}_{2}}$	7.0×10 ^{-20a}	2.5×10 ⁻¹⁹ a
$CO_3 \cdot H_2O + h\nu \rightarrow O^- \cdot H_2O + CO_2$	2.9×10 ⁻²⁰⁶	6.4×10 ^{-20 в}
$CO_3 \cdot H_2O + hv \rightarrow CO_3 + H_2O$	9.0×10 ^{-19ь}	1.0×10 - 18 в

*Reference 16.

^bRelative to the CO_3^- cross section.



FIG. 3. Photodissociation of $CO_3^- \cdot H_2O$ to give $O^- \cdot H_2O + H_2O + CO_2$ at 514 nm and a laser polarization of 54.7^{*}. (a) Laboratory kinetic energy distribution. (b) Center-of-mass kinetic energy distribution of the products.

$$E_{av} = hv - D(CO_2 - O^{-} \cdot H_2O) + E_{int}, \qquad (1)$$

where hv is the photon energy, $D(CO_2 - O^- \cdot H_2O)$ is the bond dissociation energy to form $O^- \cdot H_2O/CO_2$ products, and E_{int} is the initial internal energy of the cluster ions. E_{av} values listed in Table II were calculated assuming $D(CO_2 - O^- \cdot H_2O) = 1.58$ eV (see Sec. IV) and $E_{int} = 0.025$ eV. (We have assumed $E_{int} = 0.025$ eV since the parent $CO_3^- \cdot H_2O$ cluster ions experience an average of several hundred thermalizing collisions before exiting the source.)

TABLE II. Average kinetic energy release values, E_i , for $CO_3^- \cdot H_2O + h\nu \rightarrow O^- \cdot H_2O + CO_2$.

Photon	Available	
energy	energy ^a	E_{i}
(eV)	(eV)	(eV)
2.41	0.80	0.084
2.54	0.93	0.091
2.71	1.10	0.110

^a Defined by Eq. (1) in the text.

The average kinetic energy release values are similar to kinetic energy release values obtained from two other photodissociation processes investigated in our group.⁴

$$\mathrm{CO}_{3}^{-} \cdot \mathrm{H}_{2}\mathrm{O} + h\nu \to \mathrm{CO}_{3}^{-} + \mathrm{H}_{2}\mathrm{O}, \qquad (2)$$

$$\operatorname{CO}_{3}^{-} \cdot \operatorname{CO}_{2}^{-} + h\nu \to \operatorname{CO}_{3}^{-} + \operatorname{CO}_{2}^{-}.$$
 (3)

Unlike these latter systems, however, the photoproduct's kinetic energy values for $O^- \cdot H_2 O/CO_2$ products are dependent on the photon energy employed. Approximately 10% of the available energy is partitioned into relative translational energy of the $O^- \cdot H_2 O$ photoproduct at each wavelength measured.

C. Product angular distributions

The product angular distribution can be expressed as^{15,18,19}

$$P(\theta) = (4\pi)^{-1} [1 + \beta P_2 (\cos \theta)], \qquad (4)$$

where $P(\theta)$ is the probability that the products fragment into the solid angle ω at an angle θ with respect to the laser electric vector, P_2 (cos θ) is the second degree Legendre polynomial in cos θ , and β is a parameter that indicates the degree of anisotropy present in the dissociation and depends on the orientation of the transition dipole moment with respect to the dissociation axis. The values of β fall between -1 and 2, with positive values indicating a parallel photoabsorption process (transition dipole moment along the intermolecular axis), negative values a perpendicular process (transition dipole moment perpendicular to the intermolecular axis), and zero an isotropic dissociation.

To observe the maximum effects of photofragment anisotropy, product peaks were collected at electric vector polarizations of 0° and 90°. Representative data for $CO_3^- \cdot H_2O$ dissociating to $O^- \cdot H_2O + CO_2$ at a photon energy of 2.41 eV is shown in Fig. 4. The 0° and 90° peaks are nearly identical. The value of β extracted from this data is very close to zero throughout the range of relative kinetic energies of the separating photofragments. This result indicates that the



FIG. 4. Laboratory kinetic energy distributions for the $O^- \cdot H_2 O + CO_2$ product channel at 514 nm and laser polarizations of 0° and 90°.

photoexcited cluster ion lifetime before dissociation is much longer than a rotational period; i.e., $\tau \ge 10^{-12}$ s.

D. Calculational methods and results

The calculations on O⁻•H₂O were carried out *ab initio* on a VAX 8650 computer with use of the GAUSSIAN 82 and GAUSSIAN 88 series of programs.^{20,21} Fully optimized geometries were obtained at the MP2/6-31G** and MP2/6-31 + G* calculational levels employing analytical gradients²² and the frozen-core approximation.²³ Bond lengths were optimized to 0.001 Å and bond angles to 1°. Both linear (open) and bifurcated hydrogen-bonded systems were examined. Normal-mode vibrational frequencies were computed with the MP2/6-31G** and MP2/6-31 + G* equilibrium structures.

Planar and nonplanar structures were investigated for the open and bifurcated hydrogen-bonded systems. For both the planar and nonplanar forms, we determined 1) whether the nonhydrogen-bonded hydrogen H atom in the linear complexes is *cis* or *trans* to the O⁻, and 2) whether the O-H bond lengths remain symmetric in the bifurcated complexes. The most stable MP2/6-31G** and MP2/6-31 + G* linear and bifurcated structures are depicted in Fig. 5. Total energies (E_t , a.u.) and zero-point energies (ZPE, eV) are also included in the figure. The linear geometry is more stable than the bifurcated geometry regardless of basis set.

For both calculational levels, the linear (open) hydrogen-bonded complex has C_s symmetry with the nonhydro-





FIG. 5. Linear and bifurcated optimized geometries calculated at the MP2/6-31G** and MP2/6-31 + G* levels. Total energies and zero-point energies are included.

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gen-bonded hydrogen H atom *cis* to the O⁻. Calling this complex linear is not strictly correct, since H₂ is 3–4° above the O···O axis. While the O–H bond distance lengthens for the hydrogen-bonded hydrogen H atom compared to the distance in H₂O, H atom is not transferred to the O⁻. The MP2/6-31G** O–H bond length for H₂O is 0.961 Å; the MP2/6-31 + G* bond length is 0.971 Å. The bifurcated form has C_{2v} symmetry at the MP2/6-31G** level, which is reduced to C_s symmetry at the MP2/6-31 + G* level. For the latter computation, the O⁻ is about 1° out of the plane of the water molecule and the O···H bonds are asymmetric by about 0.001 Å.

For the linear complex, diffuse functions shorten the O_1-H_1 bond, lengthen the O_1-H_2 bond, lengthen the $H_1 \cdots O_2$ bond, and decrease the $H_1 O_1 H_2$ angle. For the bifurcated complex, diffuse functions lengthen the $O_1-H_{1,2}$ bonds, lengthen the $O_2 \cdots H_{1,2}$ bonds, and increase the $H_1 O_1 H_2$ angle.

IV. DISCUSSION

A drift tube mass spectrometer and an argon ion laser were used by Moseley and co-workers⁵ to conduct the first photon interaction studies with $CO_3^- \cdot H_2O$ at discrete photon energies between 2.35 and 2.71 eV. Assuming bond energies $D(CO_2 - O^-)$ of 2.0 ± 0.2 eV and $D(CO_3^- \cdot H_2O^-)$ of 0.5 eV, they thought it energetically possible for $CO_3^- \cdot H_2O$ to photodissociate into three product channels: $CO_3^ + H_2O$, $O^- \cdot H_2O + CO_2$, and $CO_2 + O^- + H_2O$. Their results, however, strongly indicated that the major product of $CO_3^- \cdot H_2O$ photodissociation in this wavelength region was $CO_3^- + H_2O$ and that little or no $O^- \cdot H_2O$ or O^- photofragment ions were present.

The absence of the O⁻/CO₂/H₂O photoproduct can be explained by considering the photon energies employed and the recently determined bond energies of both CO₃⁻ and CO₃⁻·H₂O. Our earlier study⁴ indicated that the least energetic dissociation channel of the core CO₃⁻ ion, the production of O⁻ and CO₂ fragments, occurs at an energy of 2.27 eV, not 2.0 eV as was previously thought.²⁴ Further, Keesee *et al.* have found water molecules and core CO₃⁻ ions to be bound by 0.61 eV.¹⁰ From these numbers, O⁻ photoproduct formation would require at least 2.88 eV. Single photon excitation in the range of wavelengths used for this experiment provide a maximum of 2.71 eV. Thus, the CO₂ + O⁻ + H₂O channel is inaccessible at these energies.

An analogous argument cannot be made to rule out $O^- \cdot H_2 O$ as a potential photoproduct. According to thermodynamic determinations, $O^- \cdot H_2 O$ is energetically feasible from parent $CO_3^- \cdot H_2 O$ cluster ions at the photon energies employed here. Although no reactions of $O^- \cdot H_2 O$ were directly observed, reactions (5) and (6)

$$O^{-}(H_2O) + O_2 \rightarrow O_3^{-} + H_2O$$
 (5)

$$O^{-}(H_2O) + H_2O \rightarrow OH^{-}(H_2O) + OH$$
 (6)

were assumed by Fehsenfeld *et al.* in order to explain observed reactions of O^- and H_2O in their flowing afterglow

experiments.¹¹ From these reactions, an upper limit of 1.3 eV for $D_0^0(H_2O - O^-)$ was deduced. Using the relation:

$$D_0^0(H_2O - CO_3^-) + D_0^0(CO_2 - O^-) - D_0^0(H_2O - O^-)$$

= $D_0^0(O^- \cdot H_2O - CO_2)$ (7)

and the dissociation values above, a lower limit of $D_0^0(O^- \cdot H_2 O - CO_2) > 1.58 \text{ eV}$ is calculated. Consequently, the $O^- \cdot H_2 O + CO_2$ product channel is energetically accessible at the photon energies employed here, in line with our experimental observations.⁵

One possible reason why $O^- \cdot H_2 O$ was not observed in the drift tube experiments may be the sensitivity. Photodissociation of $CO_3^- \cdot H_2 O$ yields only a few percent $O^- \cdot H_2 O$ ionic product with a quite small cross section (Table I). A second, and more likely explanation, is that $O^- \cdot H_2 O$ reacts rapidly in the presence of CO_2 with reaction rate constants on the order of 8×10^{-10} cm³/s.²⁵ Consequently, any $O^- \cdot H_2 O$ photoproduct could react in the high pressure region of the drift tube prior to detection. In our apparatus, photodissociation occurs in a virtually collision free environment, ($p < 10^{-9}$ Torr) eliminating the possibility of reactions after photodissociation.

The data presented thus far leads to some immediate conclusions about the dynamics of $CO_3^- \cdot H_2 O$ photodissociation. The extremely low kinetic energy release suggests that the upper state accessed by the photon is bound rather than repulsive. This statement is further supported by the isotropic angular distribution and the nearly zero β value, which indicate that the lifetime of the photoexcited cluster ion is substantially longer than a rotational period. The small kinetic energies of the photoproducts also suggests that much of the available energy, beyond that necessary to break the cluster bond, is deposited into internal energy of the dissociating fragments.

To examine the deposition of internal energy among the photofragments in greater detail, the experimental kinetic energy release data were modeled using statistical phase space theory.²⁶ In order to perform the calculation, all of the species involved must be characterized according to their fundamental vibrational frequencies and rotational constants. In addition, the differences in the zero-point energies between the parent ion and various transition states involved must be known. For orbiting ion-molecule transition states, the polarizability of the neutral is also required. When values for these parameters cannot be acquired directly from the literature, reasonable estimates can be obtained by inspection of the data available on similar species. Vibrational frequencies and rotational constants have already been established for the neutral fragment CO₂,²⁷ but are not known experimentally for the $O^- \cdot H_2 O$ anion. We used the vibrational frequencies and rotational constants calculated here for O⁻·H₂O (and reported in Table III).

The theoretical kinetic energy release distributions were relatively insensitive to the magnitude of vibrational frequencies and rotational constants and therefore a detailed knowledge of the various geometries involved was not crucial to obtaining reasonable energy distributions. The distributions were, however, strongly dependent on the total ener-

TABLE III. Parameters used in the phase space theory calculations.

Parameters	O ⁻ ·H ₂ O	CO2		
v ^a ₁ (cm ^{- 1})	300 ⁸	1338 ^h		
	525 ⁸	677 ^h		
	946 ⁸	667 ^h		
	1748 ⁸	2349 ^h		
	2355 ⁸			
	3815 ^g			
B ^b (cm ⁻¹)	1.1844 ⁸	0.673 ^h		
α^{c} (A ³)		2.59 ⁱ		
μ^{d} (amu)		19.2		
D_0^c (eV)		1.6 ⁱ		
B_{dim}^{f} (cm ⁻¹)		0.087 ^k		

Vibrational frequencies.

^bRotational constant.

^e Polarizability of neutral.

d Reduced mass.

^eDissociation energy.

^fRotational constant of cluster ion.

*Calculated as described in the text.

^hReference 27.

'Reference 28.

Calculated thermodynamically.

^k Calculated assuming a bond length of 2.0 Å.

gy available to the dissociating complex and hence to the energy differences between parent and fragment ions. This quantity was used as a parameter and was varied until the best fit with experiment was obtained. Theoretical and experimental distributions for a photon energy of 2.41 eV are compared in Fig. 6.

Excellent agreement between theory and experiment results for the $O^- \cdot H_2 O + CO_2$ channel when the entire 0.80 eV of energy available to $CO_3^- \cdot H_2 O$ is assumed statistically distributed in the dissociating cluster ion. This suggests that the thermodynamically calculated energy difference (1.58 eV) between the $O^- \cdot H_2 O + CO_2$ product and parent ion is approximately correct. Also, complete energy randomization supports the conclusion from the angular dependence



FIG. 6. Product center-of-mass kinetic energy distribution for the photodissociation of CO_3^{-} \cdot H_2O to give O^{-} \cdot $H_2O + CO_2$. The phase space theory results assume all of the available energy is statistically distributed in the products.

studies that the dissociation leading to $O^- \cdot H_2 O + CO_2$ occurs via a slow process on the molecular rotation time scale.

To summarize, photoexcitation of $CO_3^- \cdot H_2O$ leads to two sets of products. The CO_3^-/H_2O channel dominates and accounts for ~95 ± 4% of the products observed. A detailed study of this channel indicated⁴ that CO_3^- acted as a chromophore and that intramolecular energy transfer from the resultant vibrationally excited CO_3^- moiety to the $CO_3^- \cdot H_2O$ cluster was the rate determining step in the dissociation of the cluster leading to CO_3^- (H₂O) products. This mechanism accounted for the interesting observation that the CO_3^- product ion carried away ~1.4 eV of the energy available as vibration while the remaining 0.4 eV was statistically distributed.

The O⁻•H₂O channel is minor, accounting for only $5 \pm 4\%$ of the products. This channel appears to dissociate from a long lived cluster state and all available energy is statistically distributed in the products.

The question is, how do the two product channels compete? It appears almost certain that a single isomeric $CO_3^- \cdot H_2 O$ cluster is absorbing the photon. A possible mechanism that is consistent with the results for both product channels is given below:

$$CO_{3}^{-} \cdot H_{2}O + h\nu \rightarrow (CO_{3}^{-})_{elec}^{*} \cdot H_{2}O$$

$$[CO_{3}^{-} \cdot H_{2}O]_{elec}^{*} \cdot H_{2}O$$

$$[CO_{3}^{-} \cdot H_{2}O]_{elec}^{*} \rightarrow O^{-} \cdot H_{2}O + CO_{2}$$

$$(CO_{3}^{-})_{vib}^{*} \cdot H_{2}O \rightarrow (CO_{3}^{-})_{vib}^{*} + H_{2}O$$
Scheme I

The photon is initially absorbed into an electronic state primarily localized on the CO_3^- moiety. Two things can then happen. About 5% of the time the system internally converts to an electronic excited state of the cluster. This cluster then vibrationally predissociates to $O^- \cdot H_2 O/CO_2$ products on a time scale short compared to photon emission to the electronic ground state of the cluster. Most of the time, however, the system internally converts to the CO_3^- ground state that is now strongly vibrationally excited. This state eventually dissociates to $CO_3^- / H_2 O$ with substantial vibrational energy remaining in the CO_3^- product. Such a mechanism is fully consistent with the previously published work on photodissociation of CO_3^- and $CO_3^- \cdot H_2 O$. It also fully explains the new data presented here on the $O^- \cdot H_2 O/CO_2$ product channel.

An alternative mechanism for the $O^- \cdot H_2 O/CO_2$ channel is possible. The $(CO_3^-)_{elec}^* \cdot H_2 O$ state initially formed by photon absorption could directly dissociate to $O^- \cdot H_2 O/CO_2$ products. This dissociation would then be in competition with internal conversion to form $(CO_3^-)_{vib}^* \cdot H_2 O$ that eventually leads to $CO_3^- / H_2 O$ products. This option is attractive in that the photodissociation cross section for $O^- \cdot H_2 O/CO_2$ production is very similar in magnitude to O^- /CO_2 photoproduction from CO_3^- (see Table I). A

drawback to this mechanism is the fact that $O^- \cdot H_2 O/CO_2$ products are formed by statistical vibrational predissociation while the O^-/CO_2 products are formed by electronic predissociation.²⁴ Consequently, the mechanism shown in Scheme I was chosen.

Direct formation of a bound $[CO_3^- \cdot H_2 O]_{elec}^*$ state by photon absorption followed by vibrational predissociation to $O^- \cdot H_2 O/CO_2$ products was also considered. Such a mechanism partitions the ultimate products in the photon absorption step rather than following photon absorption. This mechanism was not chosen because the Franck–Condon factors to this state should be very small since the photon is absorbed well above the dissociation asymptote.

Finally, formation of $O^- \cdot H_2 O/CO_2$ from $(CO_3^-)_{vib}^*$ $\cdot H_2 O$ was ruled out because complete randomization of all of the vibrational energy would be required and from our earlier work⁴ on the $CO_3^-/H_2 O$ product channel we know this is not the case.

V. CONCLUSIONS

(1) Photodissociation of $CO_3^- \cdot H_2 O$ in the visible wavelength range forms $O^- \cdot H_2 O/CO_2$ products about $5 \pm 4\%$ of the time. The dominant product is $CO_3^-/H_2 O$.

(2) The $O^- \cdot H_2 O/CO_2$ products are formed from statistical vibrational predissociation of a bound state. Consideration of all of the data for both product channels suggests the state leading to this product is an electronically excited state of the cluster. In contrast, the CO_3^-/H_2O products come from the ground state.

(3) Ab initio electronic structure calculations were performed. These indicated $O^- \cdot H_2 O$ is a quasilinear molecule, with one of the protons of the water molecule bridging the O^- oxygen and the water oxygen.

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