section data are shown for comparison.

It appears from the large cross sections and long lifetime observed for D_2^- that these species may be in a quartet electronic state analogous to that of He^- $(1s2s2p)^4P_j$.

Calculations on H_3^- indicate that this ion is unstable with respect to $H_2 + H^-$ clustering.[10] The similarity between the D_3^- and D_2^- attenuation cross sections indicates that D_3^- may also be electronically excited.

The isotopic and pressure effects on the relative production efficiency of the diatomic and triatomic hydrogen negative ions are being studied further in order to elucidate the mode of formation of these species.

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Photodissociation Spectrum of CO₃⁻: Evidence for a Bound Excited State*

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The photodissociation cross section for $CO_3^- + h\nu \rightarrow CO_2 + O^-$ has been measured from 6400 to 5650 Å using a drift-tube mass spectrometer and a continuously tunable dye laser. The cross section has very detailed structure, which is interpreted as reflecting the vibrational levels of a bound, predissociating state of CO_3^-.

The existence of bound excited states for negative ions is the subject of considerable current interest. Autodetaching states of atomic negative ions have been discussed in several recent Letters,[1-4] and such a state has also been observed for a molecular ion.[5] Molecular negative ions, particularly those with a large electron attachment energy, may have bound excited states that do not autodetach. Such a state has been observed[6] in C_2^-, and one probably exists[7,8] in O_3^-. We report here on the observation of a bound excited state in CO_3^- by measurement of the photodissociation cross section of this ion.

The experimental apparatus, consisting of a drift-tube mass spectrometer and a laser, is basically the same as that previously[9,10] used to measure the photodissociation cross section for CO_3^- at seven discrete wavelengths between 5287

and 4579 Å. However, the argon-ion laser used in that work has been replaced by a tunable dye laser having a resolution of 0.5 Å. The CO_3^- ions are formed by reaction[9,10] between O^- and CO_2, and drift under the influence of a weak applied electric field through CO_2 gas toward an extraction aperture. The ratio of the electric field strength to the neutral-gas density, E/N, is chosen such that the directed drift velocity is only about one tenth the mean thermal speed of the ions and gas molecules at room temperature. Thus, the ions experience a large number of thermalizing collisions following their production. Just before passing through the extraction aperture, the ions intersect the intracavity photons of the dye laser, which is chopped at 100 Hz.

The ions which pass through the extraction aperture are mass selected by a quadrupole mass

spectrometer and individually detected by an electron multiplier. By counting these ions for alternate periods when the laser is on and when it is off, the cross section for the loss of a particular ion species due to photon interaction, the photodestruction cross section, can be determined.[9,10] Such photodestruction may be due to photodetachment, photodissociation, or both. It is also possible that two-photon processes and collisional dissociation following photon excitation to a loosely bound state could contribute, but we have not yet observed any such processes. By tuning the mass spectrometer to the appropriate mass, the photofragment ions resulting from photodissociation can also be observed, and the photodissociation cross section measured.

In previous work,[9,10] we established that between 5287 and 4579 Å the primary photodestruction process for CO_3^- was the photodissociation reaction

$$CO_3^- + h\nu \rightarrow CO_2 + O^- , \qquad (1)$$

and that the photodetachment threshold for CO_3^- was probably at an energy of at least 2.7 eV. Figure 1 shows the results of similar measurements on the destruction of CO_3^- over the range from 6400 to 5650 Å made using the tunable laser. These data were obtained at E/N values of 10 and 20 Td (1 Td = 10^{-17} V cm^2), at which the CO_3^- drift velocities are (4.0 and 8.0)×10^3 cm/sec, respectively. The gas pressures used were 0.05 Torr of CO_2, and 0.1 Torr of 1:1 mixture of CO_2 and O_2. The drift distance was 10.1 cm or greater. Absolute cross-section values were determined by normalization to previously measured

O^- (Branscomb et $al.$[11]) and O_2^- (Ref. 8 and Burch, Smith, and Branscomb[12]) photodetachment cross sections, using techniques discussed in Refs. 8–10. Photofragment O^- ions were observed over the entire wavelength range, and no other photofragment ions were observed. The uncertainty in the absolute value of the cross sections is ±25%. The error bars in the figure represent the uncertainty in the relative cross-section values.

The large number and close spacing of the maxima observed in the CO_3^- photodissociation cross section suggest that as a result of photon interaction, the ions undergo transitions to a bound excited state which dissociates into $O^- + CO_2$. The observation of O^- photofragment ions indicates that photodissociation is occurring, but a two-photon photodestruction or photon excitation followed by collisional dissociation could conceivably also be present. Further, if the parent CO_3^- ions have substantial vibrational excitation, these excited levels could contribute to the observed structure. To resolve these questions, several additional experiments were performed.

First, it was important to establish that the major photodestruction process was photodissociation into $O^- + CO_2$. The relative cross section for the appearance of O^- photofragments was measured at fourteen wavelengths corresponding to the major maxima and minima in Fig. 1, and normalized at 5990 Å. The resulting cross sections were in excellent agreement with those of Fig. 1, indicating that most, if not all, of the observed photodestruction is due to the photodissociation reaction (1).
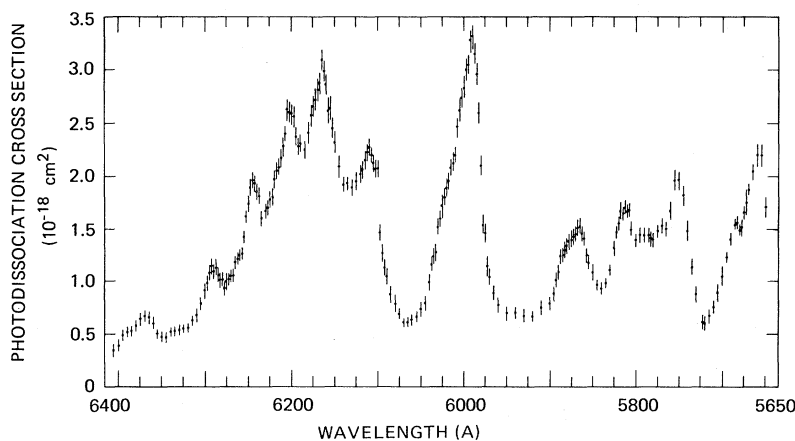

FIG. 1. Total photodestruction cross section for CO_3^- as a function of wavelength, obtained by observation of the loss of CO_3^-. The photodestruction process was identified to be photodissociation, $CO_3^- + h\nu \rightarrow CO_2 + O^-$, by observation of the O^- photofragments.

The possibility of collisional dissociation was investigated by searching for a dependence of the cross section on either CO_2 pressure or collision energy. The pressure studies covered a range from 0.040 to 0.100 Torr at an E/N of 10 Td, thus changing the number of collisions experienced by an ion after passing through the photon beam by a factor of 2.5 while keeping the average collision energy nearly thermal. At 0.050 Torr, E/N was increased to 50 Td, which doubled the mean collision energy. In both cases, the cross section was observed to remain constant. The possibility of two-photon processes was investigated by varying the intracavity laser power from approximately 5 to 130 W at 5990 Å, and by variations of approximately a factor of 5 at several other wavelengths. The cross section was observed to remain constant in each case. Thus, it is concluded that collisional dissociation and two-photon processes do not play a significant role in the photodestruction under our experimental conditions.

Finally, the possible effect of vibrational excitation of the parent CO_3^- ions on the measured cross sections was investigated. These ions are likely to be formed vibrationally excited and the number of thermalizing collisions required for them to reach vibrational equilibrium at room temperature is not known. Therefore, the cross section was measured at several wavelengths as the drift distance was increased from 2.54 to 20.3 cm, increasing the number of thermalizing collisions from about 125 to 1000. For distances shorter than 5.08 cm, a slight increase (10–20%) in the cross section was observed, but for longer drift distances the cross section was constant. As mentioned earlier, all of the data presented in Fig. 1 were taken at drift distances of 10.1 cm or greater. The shape of the cross section between 5990 and 6290 Å was measured at collision energies from those corresponding to room temperature up to a mean collision energy of 0.2 eV. Such an increase in mean collision energy between the CO_3^- and CO_2 molecules would be expected to result in substantially increased vibrational excitation of the CO_3^-. However, no change in the shape of the cross section was observed. This result is surprising, since if vibrationally excited states become involved in the photodissociation, changes in the structure should be observed. These measurements were not as detailed as those of Fig. 1, and it is possible that slight changes in the structure were missed. It is also possible that the vibrational temperature

of the CO_3^- was much lower than their kinetic temperature, and consequently the amount of vibrational excitation was small. In any case, we conclude that the effect of vibrational excitation of the parent molecule on either the absolute magnitude or the shape of the cross section presented in Fig. 1 is negligible. Recall that the data of Fig. 1 were all obtained for very low CO_3^- drift velocities, and hence at essentially room temperature.

The overall conclusion of these studies is that the results presented in Fig. 1 are characteristic of an excited state (or states) of CO_3^- which has a sufficiently deep potential well to accomodate a number of vibrational levels, and which lives for a time substantially longer than one vibrational period. Further, CO_3^- in this state spontaneously breaks up into $CO_2 + O^-$.

The photodissociation cross sections of Fig. 1 contain basically the same kind of information obtainable for neutral molecules from absorption spectra. It is not generally possible to obtain a sufficient number density of ions in the gas phase to allow the usual absorption techniques to be used. The absorption spectra of ions has generally been studied by isolating them in solid matrices, but these experiments are often difficult to interpret and are subject to the uncertainty of the influence of the matrix environment on the ion. The infrared spectrum of CO_3^- has been studied[13] in this way.

The observed dissociation could be caused by a curve crossing to a dissociative state, or by a change in the geometric configuration of the molecule. In all likelihood, geometric considerations impede the direct photodissociation of CO_3^-. The ground state of CO_2 is linear, while the ground state of CO_3^- is believed to be a trigonal structure of C_{2v} symmetry,[13] with an O-C-O bond angle of nearly 120°. In the initial excited configuration the molecule is probably trigonal, and if so, there will be an effective barrier against direct dissociation. As the excited molecule vibrates, for example, in the ν_3' or ν_4' bending modes, the O-C-O bond angle could approach 180°, thus facilitating dissociation. The close spacing of the peaks in the envelope centered near 6200 Å indicates that these peaks characterize a weak vibrational mode, such as ν_3' and ν_4' are likely to be.

Obviously, it would be of interest to use the spectroscopic information contained in Fig. 1 to characterize the excited CO_3^- state. This is difficult because of the limited wavelength range of

the data. However, it is known from our previous work[9,10] that CO_3^- continues to absorb and photodissociate at wavelengths as short as 4579 Å, and very probably at even shorter wavelengths. Further, there is evidence[14] that CO_3^- continues to photodissociate at longer wavelengths to at least 6800 Å, and that a very strong absorption exists near 6600 Å. It therefore seems feasible that the photodissociation cross section of this molecule can be obtained from 6800 Å to below 4579 Å. This should provide a sufficient range to determine the vibrational frequencies of this excited state, as well as other information concerning its character.

The visible absorption spectrum has been reported[15] for the NO_3 molecule which is isoelectronic to CO_3^-. Approximately twenty diffuse bands were observed in this spectrum between 6650 and 5000 Å. The absorptions were assigned[15] to the transition[16]

$$(e')^3(a_2')^2, {}^2E' \leftarrow (e')^4(a_2'), {}^2A_2' , \qquad (2)$$

and the diffuseness of these bands interpreted as indicating a predissociation of this molecule in the excited state. However, the high density and general diffuseness of the bands permitted vibrational assignment only to ν_1'. A detailed study of the CO_3^- photodissociation spectrum should also provide information complementary to that in the NO_3 absorption spectrum, thus assisting in characterization of the states of each species.

The technique used here will be applicable to any molecular ion which absorbs in the range of available high-power tunable lasers, and which can be made to undergo a dissociation soon after absorption. We have observed[8,10] the photodestruction of $CO_3^- \cdot H_2O$, O_3^-, and O_4^-. Indications are that each of these cross sections exhibits variations with photon energy related to the structure of the ions. The ability of this technique of photodissociation spectroscopy to specify the absorbing species, vary its internal energy

content, and identify charged photofragments promises to assist significantly in understanding the structure of complex molecular ions.

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