analysis.²⁰ The distribution of scatterers was in all cases fairly monodisperse, and from the thus determined diffusion coefficient we calculated via the Einstein-Stokes relationship an equivalent hydrodynamic radius $R_{\rm H}$. $R_{\rm H}$ was found to be very sensitive to preparation and handling techniques and varied from one sample to another in the range 150 Å $< R_{\rm H} < 250$ Å. One of the possible causes might be impurities in the water as evidenced by the observation that preparation with distilled but not deionized water

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leads to the formation of large (several thousand angstroms) aggregates. We have not been able to detect any significant amount of scatterers with $R_{\rm H} < 100$ Å. We are thus led to postulate that in addition to the distribution of small colloids seen in transmission electron micrographs there are additional particles in the 200-Å range. Since the amount of light scattered in the Rayleigh regime varies like the square of the volume, one diskshaped particle with $R_{\rm H} = 200$ Å scatters as much light as 10000 particles with $R_{\rm H} = 20$ Å, which might explain why a small number of larger particles can pass unnoticed in the TEM histogram analysis and yet dominate the light scattering signal.

An Electronic Absorption Spectrum of C_2^+ : $\tilde{B}^4 \Sigma_u^- \leftarrow \tilde{X}^4 \Sigma_a^-$

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The $\tilde{B}^{4}\Sigma_{u} \leftarrow \tilde{X}^{4}\Sigma_{g}^{-}$ electronic transition of C_{2}^{+} in a 5 K neon matrix has been identified. The 0–0, 1–0, and 2–0 bands are observed in absorption when ${}^{12}C_{2}^{+}$ and ${}^{13}C_{2}^{+}$ are produced in the matrix by photolysis followed by photoionization of various precursors, the most favorable one being chloroacetylene. The carrier and symmetry of the transition are assigned on the basis of spectroscopic and chemical evidence and by comparison to recent calculations. The 1-1 band is also observed in the wavelength-dispersed fluorescence spectrum of C_2^+ , subsequent to laser excitation of the 1–0 absorption transition. The derived spectroscopic constants (in neon matrix) are $v_{00} = 19765$ (4) cm⁻¹, $\omega_e' = 1507$ (4) cm⁻¹, $\omega_e x_e' = 8$ (4) cm⁻¹, and $\nu''(1-0) = 1359$ (6) cm⁻¹.

Introduction

The open-shell ion C_2^+ is one of the few simple, fundamental species whose spectroscopy remains virtually unknown or uncertain. This is in spite of the assumed importance of C_2^+ in comets, in chemical schemes for the formation of hydrocarbons in interstellar media, and in plasma reactions.¹ Of the two spectroscopic studies dealing with C_2^+ , one assignment² has been questioned in view of the two theoretical calculations carried out,^{3,4} whereas the other one was a low-resolution approach.⁵

An absorption spectrum (at 249 nm) observed in a flash discharge of acetylene was assigned to a ${}^{2}\Sigma_{g}^{-} \leftarrow {}^{2}\Pi_{u}$ transition of $C_{2}^{+,2}$ However, as the ground state of C_{2}^{+} has the symmetry ${}^{4}\Sigma_{g}^{-}$, the transition would have to be between excited electronic states of C_2^+ . Unfortunately, in neither of the two theoretical works^{3,4} is there a satisfactory match with the experimental observation.

A recent translational energy loss spectrum of C_2^+ showed several broad bands,⁵ which were attributed to electronic transitions within the quartet and doublet manifolds by comparison to the calculated state energies.³ Thus, the most detailed information at present still stems from the two computational efforts.^{3,4}

In this contribution we present the spectrum of the $\tilde{B}^{4}\Sigma_{u}^{-}$ $\tilde{X}^{4}\Sigma_{g}^{-}$ electronic absorption of C_{2}^{+} embedded in a 5 K neon matrix and the evidence for the assignment. The waveguide absorption technique, which has proved successful in the characterization of parent open-shell molecular ions,^{6,7} was employed.

Experimental Section

Absorption measurements were carried out with a wavelength-selecting monochromator (0.1-nm band-pass), using light

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modulation and a photodiode or photomultiplier in conjunction with phase-sensitive detection and an on-line LSI 11/03 computer system.7 Use of the waveguide technique enhanced the absorption by a factor of ≈ 200 by passing the light through ≈ 2 cm of a matrix, which is 130 μ m thick.

The molecular species were embedded in the neon matrix with a dilution in the range 1:3000-1:8000. In the present experiments vacuum-UV radiation (H Ly α , 121.6 nm; Xe I, 147.0 nm) was first used to photolyze the molecular precursor to produce fragments, which were subsequently photoionized by Ne I (73.6 nm) photons. In some of the experiments, H₂O was codeposited for the purpose of acting as an electron scavenger. However, it was found that this was usually not necessary for the observation of the C_2^+ signals.

The various precursors used either were obtained commercially (HCCH, H¹³C¹³CH, DCCD, NCCN, C₂HF₃) or were synthesized according to documented procedures9 (CICCH, CICCD, CICCCI, BrCCH) and were purified by vacuum distillations.

In the laser excitation experiments a pulsed dye laser (0.02-nm bandwidth) was oriented $\approx 45^{\circ}$ to the matrix. The fluorescence was viewed along the thin side, in the same direction as in the absorption, with a monochromator and registered with gated electronics.

Results and Discussion

In Figures 1 and 2 are shown portions of the absorption spectra following vacuum-UV irradiation of 5 K neon matrices containing acetylene and chloroacetylene in dilute concentrations. No absorption bands are apparent prior to irradiation. The top traces are observed after several minutes of photolysis with either H Ly α (Figure 1a) or Xe I (Figure 2a), the purpose of which is to produce C_2 , evidenced by bands of two well-known systems of C_2 , the $D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and the $A^1\Pi_u \leftarrow X^1\Sigma_g^+$ transitions.¹⁰ With acetylene the C_2 bands are intense enough after H Ly α but barely perceptible after Xe I irradiation. Both sources lead to intense

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Figure 1. Absorption spectra obtained after irradiation of a 5 K neon matrix containing acetylene (HCCH:H₂O:Ne \approx 2:1:8000) (a) with H Ly α and (b) subsequently with Ne I photons. The assigned peaks belong to the $C_2^+ \tilde{B}^4 \Sigma_u^- \leftarrow \tilde{X}^4 \Sigma_g^-$ and $C_2^- \tilde{B}^2 \Sigma_u^+ \leftarrow \tilde{X}^2 \Sigma_g^+$ transitions. The peak denoted with an asterisk is a Hg calibration line.



Figure 2. Absorption spectra recorded after irradiation of a 5 K neon matrix containing chloroacetylene (ClCCH:H₂O:Ne \approx 2:1:8000) with (a) Xe I and (b) subsequent Ne I photons. Spectrum c (ClCCH:Ne \approx 1:8000) is observed after the irradiation sequence H Ly α + Ne I. The peaks denoted with an asterisk are Hg calibration lines.

C₂ bands with ClCCH, ClCCCl, or BrCCH, although H Ly α still seems to be more efficient. In the spectral region shown, only a few weak unassigned bands are apparent with chloroacetylene in the matrix (Figure 2), whereas with acetylene the two broad structured bands (Figure 1) are due to the known $\tilde{B}^2 \Sigma_u^+ \leftarrow \tilde{X}^2 \Sigma_g^+$ absorption system of $C_2^{-11,12}$ The production and mechanism of formation of C_2^- in rare gas matrices have been discussed.¹³

Upon subsequent irradiation with Ne I photons, three sharp bands appear (Figures 1 and 2). These bands are also observed when CICCD, CICCCl, BrCCH, NCCN or trifluoroethylene is embedded and photolyzed/ionized in the neon matrix. In the case of ClCCH, the 0-0, 1-0, and 2-0 bands of C_2^- also become apparent (Figure 2c). The unlabeled broad bands are already present after Xe I photolysis (cf. Figure 2a) and are characteristic of the precursor in the matrix. Thus, different haloacetylene precursors lead to a variation in the spectral features, the carriers of which have not been identified.

It should be noted that the new band at 505.8 nm (19765 cm⁻¹) is already seen, but weakly, upon initial Ne I irradiation, but increases after additional Xe I or H Ly α photolysis, followed by further Ne I photoionization. The new bands are also discernible by using first H Ly α photons (which produce the strong C₂ bands); however, they become intense only after subsequent Ne I photoionization.

On the basis of the following observations and arguments the new system consisting of the three sharp bands is ascribed to the $\tilde{B}^{4}\Sigma_{u}^{-} \leftarrow \tilde{X}^{4}\Sigma_{g}^{-}$ electronic transition of C_{2}^{+} .

Mercury source ($\lambda_{max} \approx 365 \text{ nm}$) irradiation results in 50–60% intensity decrease in the new band system as well as of the $C_2^$ bands; the intensity of a neutral radical band (e.g., CN) remains virtually unchanged. This suggests that the band carrier is an ion. The C_2^- bleaching is caused by photodetachment,¹² whereas with cations this has been attributed to recombination with the liberated electrons.⁶ Bleaching is also observed with Xe I and H Ly α sources; the intensity of the ionic bands is partly restored by subsequent Ne I irradiation.

The observed band system consists of one progression, suggesting a diatomic species. It does not correspond to any known transitions of possible common products obtainable from the tetraatomic precursors XCCH and XCCX (X = H, D, Cl, Br). Only directly formed fragments (e.g., C₂H, C₂X, and their ions) are likely to be produced in a detectable concentration: C_2^+ is the obvious common entity that can be formed. The ionization energy of C_2 is $\approx 12 \text{ eV}$,¹⁴ and thus the production of C_2^+ with even H Ly α (10.2 eV) is possible. Comparison of the transition energy and observed vibrational frequencies with the recent calculations^{3,4} and consideration of isotopic shifts compel the assignment of the band system to C_2^+ .

Two electronic transitions of C_2^+ are predicted in the 500-nm spectral region: the $\tilde{B}^4\Sigma_u^- \leftarrow \tilde{X}^4\Sigma_g^-$ and $f^2\Pi_g \leftarrow \tilde{a}^2\Pi_u$ transitions. Their energies are 2.47 (2.50) and 2.44 (2.23) eV, respectively, where the first values are from ref 4 and those in parentheses are from ref 3. The former values are judged by their authors to be accurate to ± 0.1 eV. In comparison, the observed origin band in the neon matrix is at 2.451 \pm 0.001 eV. Open-shell cations in neon matrices can be red-shifted by up to a few hundred cm⁻¹ from the gas-phase value.⁷ In the translational energy loss spectrum of C_2^+ the prominent peak with maximum at 2.50 eV was assigned to the $\tilde{B}^4 \Sigma_u^- \leftarrow \tilde{X}^4 \Sigma_g^-$ transition.⁵ Although the ionization of $C_2 X^1 \Sigma_g^+$ can produce both the $\tilde{X}^4 \Sigma_g^-$

and $\tilde{a}^2 \Pi_u$ states of C₂⁺, in the cold environment of the neon matrix the ions should be relaxed to their ground electronic states. For example, in the case of C₂, the Swan absorption system $(d^3\Pi_g \leftarrow$ $a^{3}\Pi_{u}$) is not observed in the neon matrix because of efficient intramolecular conversion between the two lowest electronic states $(a^3\Pi_u \longrightarrow X^1\Sigma_g^+)$ even though the coupling is formally spin and symmetry (g-u) forbidden. Such relaxation phenomena have been studied and discussed for C₂ as well as for other diatomics.¹⁵ Presumably, a similar mechanism would enhance the intramolecular relaxation in a neon matrix from the $\tilde{a}^2\Pi_u$ to the $\tilde{X}^4\Sigma_{e}^{-1}$ state of C_2^+ , which are calculated to lie ≈ 0.8 eV apart.^{3,4} This would account for the observation of only one new band system around 500 nm.

It should be pointed out that the absence of the C_2 Swan absorption in the neon matrix has proved to be crucial in the observation of the C_2^+ absorption (cf. Figures 1 and 2). In all gas-phase experiments the strong C2 Swan system dominates this spectral region, which makes the detection of other less intense systems difficult.

One can also eliminate the possible attribution of the observed band system to the $f^2 \Pi_g \leftarrow \tilde{a}^2 \Pi_u$ transition of C_2^+ because the calculated vibrational frequencies for the $\tilde{f}^2 \Pi_g$ and $\tilde{B}^4 \Sigma_u^-$ states are sufficiently different. The predicted ω_e values (±40 cm⁻¹ estimated error) are 1859 and 1507 cm⁻¹, and since the anhar-monicities are of the order of 20 and 10 cm⁻¹,⁴ the v' = 1-0 interval in the two excited electronic states is ≈ 1820 and ≈ 1490 cm⁻¹, respectively. In the 5 K neon matrix the species are in the lowest

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Figure 3. Laser-excited wavelength-dispersed fluorescence spectra from 5 K neon matrices containing C_2^+ generated by photolysis/ionization of ClCCH (a, b) or HCCH (c) precursors. The laser was set to the $1 \leftarrow 0$ (470.3 nm) transition of C_2^+ , and the fluorescence was dispersed with resolutions of 0.1 nm (a, b) and 1 nm (c). The assigned peaks are the $\tilde{B}^{4}\Sigma_{u}^{-} \rightarrow \tilde{X}^{4}\Sigma_{g}^{-}$ 1-1 transition of C_2^+ and the $\tilde{B}^{2}\Sigma_{u}^{+} \rightarrow \tilde{X}^{2}\Sigma_{g}^{+}$ 0-0 one of C_2^- . Trace d is a laser excitation spectrum of the $1 \leftarrow 0$ transition of C_2^+ obtained when the fluorescence at 502.4 nm is monitored.

vibrational level of the lower electronic state, and therefore the separations between the three peaks in the absorption spectrum (Figure 2) give the spacings of the vibrational levels in the excited state. The observed frequencies ($\pm 2 \text{ cm}^{-1}$) are 1491 cm⁻¹ (v' = 1-0) and 1475 cm⁻¹ (v' = 2-1), which yields $\omega_e' = 1507$ and $\omega_e x_e' = 8 \text{ cm}^{-1}$. Thus, the vibrational frequencies can only correspond to the $\tilde{B}^4 \Sigma_u^-$ state of C_2^+ .

Another species, CO⁺, has an electronic transition $\tilde{A}^2\Pi \leftarrow \tilde{X}^2\Sigma^+$ in this region (gas-phase origin at 491 nm). Furthermore, the vibrational frequency in the $\tilde{A}^2\Pi$ state is 1535 cm⁻¹ (gas).¹⁶ The question was therefore whether CO⁺ could be formed in the matrix as a result of impurities (H₂O is invariably present in trace amounts) and some specific photolysis-induced reactions with the acetylenes in the matrix. Consequently, CO was embedded alone and together with electron scavengers (e.g., CH₂Cl₂, H₂O) in neon matrices and subsequently photoionized. A CO⁺ absorption spectrum could not be observed.

Isotopic studies proved that CO⁺ is not the absorber and support the assignment of the band system to C_2^+ . When H¹³C¹³CH (99%) isotopically pure) was used as the precursor, the origin band was not shifted within the uncertainty of the measurements $(\pm 0.1 \text{ nm})$, whereas the $1 \leftarrow 0$ absorption peak was red-shifted (see Table I), indicating a frequency decrease from 1491 to 1434 cm⁻¹ on isotopic substitution. This is consistent only with a species containing two carbon atoms; the shift for a species with one carbon atom (e.g., CO⁺) would be significantly smaller. (The $2 \leftarrow 0$ absorption peak of ${}^{13}C^{13}C^+$ is obscured by the ${}^{13}C^{13}C^- 2 \leftarrow 0$ multisite band.) Neither new bands nor shifts of the absorption peak were discernible when $H_2^{18}O$ (61% isotopic purity) was codeposited with HCCCl as precursor. Experiments conducted with DCCD and ClCCD evidenced no changes in the absorption peaks. This excludes C_2H^+ and other simple hydrogen-containing species as possible absorbers.

Measurement of the laser-excited fluorescence spectrum of the $C_2^+ \tilde{B}^4 \Sigma_u^- \rightarrow \tilde{X}^4 \Sigma_g^-$ transition in the neon matrix, with the objective of obtaining vibrational frequencies of C_2^+ in the $\tilde{X}^4 \Sigma_g^-$ state, proved only partially successful. For the concomitantly formed C_2^- such spectra could easily be obtained.

TABLE I: Band Maxima in the Absorption and Fluorescence Spectra of the $C_2^+ \tilde{B}^4 \Sigma_u^- - \tilde{X}^4 \Sigma_g^-$ Transition^a

v'-v''	¹² C ¹² C ⁺	¹³ C ¹³ C ⁺	
0+0	505.8	505.8	
1 ← 0	470.3	471.6	
2 🕶 0	439.8		
$1 \rightarrow 1$	502.4		

^aAll values ±0.1 nm.

In these experiments, the laser was set to the maximum of the 0-0 (505.8 nm) or the 1-0 (470.3 nm) absorption peaks of C_2^+ . The fluorescence spectra consist of many relatively broad peaks (Figure 3a) that differ when acetylene or chloroacetylene is used as precursor of C_2^+ . Most of the bands have not been identified. However, the region of the expected 0-1 and 1-1 transition of $C_2^+ \tilde{B}^4 \Sigma_u^- \rightarrow \tilde{X}^4 \Sigma_g^-$ can be localized on the basis of the observed 0-0 and 1-0 band positions and by using the calculated $\tilde{X}^4 \Sigma_{o}^{-1}$ state values of $\omega_e^{\prime\prime} = 1335 \text{ cm}^{-1}$ and $\omega_e x_e^{\prime\prime} = 12 \text{ cm}^{-1.4}$ The predicted positions are thus 541.7 and 501.2 nm for the 0-1 and 1-1 bands, respectively. A common peak at 502.4 \pm 0.1 nm is present in the fluorescence spectra with ClCCH (Figure 3a,b) (or ClCCD) and HCCH (Figure 3c) as precursors when the laser excites the 1-0 transition of C_2^+ ; when the laser wavelength is tuned away from the 1-0 transition, the peak disappears. This is seen directly in an excitation spectrum obtained by scanning the laser wavelength while the fluorescence at 502.4 nm is monitored (Figure 3d). The observed excitation peak coincides with the 1-0 transition of C_2^+ in the absorption spectrum and is thus suggestive that the band at 502.4 nm is the 1-1 transition of C_2^+ . Further evidence for this is provided by studies using ${}^{13}C_2^+$ produced from H¹³C¹³CH.

On isotopic substitution, the 1–0 absorption band of the $\tilde{B}^{4}\Sigma_{u}$ $\leftarrow \tilde{X}^{4}\Sigma_{g}^{-}$ transition is shifted to 471.6 nm. When the monochromator was set to 502.4 nm (i.e., 1 \rightarrow 1 transition), a peak in the laser excitation spectrum is again observed at 471.6 nm. When the monochromator is tuned away from 502.4 nm, the peak in the excitation spectrum disappears.

Attempts to find the 0-1 band in the fluorescence spectrum when the laser pumped the 0-0 origin band were inconclusive. At the expected position, with chloroacetylene or acetylene or their isotopic derivatives, strong bands due to emitting fragment species

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are present. The 1-2 and 1-3 fluorescence bands were also not found. Thus, only the 1-1 band in the fluorescence spectrum was located, and its position as well as that of the 1-0 absorption band (Table I) yields for the separation of the v'' = 1-0 levels in the $X^4\Sigma_g^-$ state of C_2^+ a frequency of 1359 ± 6 cm⁻¹. In conclusion, it should be possible to identify and investigate

 C_2^+ , for example in comets, by means of the reported $\tilde{B}^4 \Sigma_u^- \leftarrow \tilde{X}^4 \Sigma_g^-$ transition. The spectrum should be relatively rich, like that of C_2 , because cooling by IR radiation is dipole forbidden. C_2^+ has recently been shown to be a constituent of two comets by the in situ mass spectroscopic measurements.17,18

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A further experiment that would characterize C_2^+ would be an ESR study of the quartet ground electronic state in a neon matrix. This approach has been used with success on a number of small open-shell cations.¹⁹ Our efforts are aimed at observing the spectrum and the rotational structure of the $\tilde{B}^4 \Sigma_u^- - \tilde{X}^4 \Sigma_g^$ transition of C_2^+ in the gas phase.²⁰

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(20) Note Added in Proof. The gas-phase spectrum has now been observed: Rösslein, M.; Wyttenbach, M.; Maier, J. P. J. Chem. Phys., in press.

Effective Dissociation Cross Section for the Low-Energy (0.5–31 eV) Electron Impact on Solid *n*-Hexane Thin Films

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We describe a low-energy electron impact experiment, performed on thin n-hexane films held at 80 K, that was designed for the measurement of the effective dissociation cross section in the energy range 0.5-31 eV. The onset of dissociation was found at \approx 3.6 eV incident electron energy, implicating the excitation of a low-lying triplet state. High dissociation rates at electron energies close to the ionization threshold were correlated to dissociative excited singlet and superexcited states.

The quantization of radiation damage on organic liquids and solids has often been an ultimate objective in radiation physics in connection with the fields of radiation chemistry, radiobiology, electron microscopy, and spectroscopies of high-energy particles. Since low-energy (0-50 eV) electrons are a main agent that distributes the energy of ionizing radiations,¹ specific measurements using them as source particle are needed to characterize the degradation process. In fact, measurements of low-energy electron scattering cross sections or electron attenuation lengths are generally made in view of their possible application in modeling studies of radiation effects.^{2,3} At this stage, the radiation damage is introduced through the relevant energy-dependent probabilities (quantum yields) of dissociation (or product formation) for every electron-scattering event. Such information is highly fragmentary in condensed phases, whereas that obtained from gas-phase experiments does not appear transferable since several mechanisms are modified (or appear) in condensed phases.⁴⁻⁷ Finally, calculations from first principles are virtually impossible.

We briefly describe in this Letter an experimental method to directly measure radiation damage caused by low-energy electrons. Our results provide the first experimental estimate of an effective dissociation cross section for low-energy electron impact on an organic solid. We investigated *n*-hexane thin films at 80 K bombarded with 0.5-31-eV electrons.

Experiment

The method is a combination of temperature-programmed desorption (TPD) and low-energy electron transmission (LEET)⁸ techniques. A thin film of the solid investigated is deposited in

vacuo from condensation of the vapor on a metallic substrate held at 80 K and bombarded for a time t with a radially symmetric electron density $J_0(r)$. Afterwards, the target is heated to sublime the film near the entrance of a mass spectrometer (MS) tuned on the mass of the condensed molecule. The integrated mass peak signal is proportional to the number of molecules $N^{T}(t)$ which remain intact during bombardment. $N^{T}(t)$ is a sum of decreasing exponential functions of time, superimposed on constant signal N^{R} (eq 1). With the knowledge of $J_{0}(r)$, one can deduce from

$$\left[\frac{N^{\mathrm{T}}(t)}{N^{\mathrm{T}}(0)}\right] = \int_{0}^{R} \frac{2\pi r}{\pi R^{2}} \exp\left[-\frac{\sigma_{\mathrm{D}} J_{0}(r) t}{e}\right] \mathrm{d}r + \left[\frac{N^{\mathrm{R}}}{N^{\mathrm{T}}(0)}\right]$$
(1)

the exponential argument the value of the effective dissociation cross section $\sigma_{\rm D}$. In eq 1, R is the beam radius and e the ele-

J. J. Geophys. Res. 1987, 92, 39.

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