Stability of the Ground State Vinylidene Anion H_2CC^-

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A technique to measure very low collisionless decay rates of ionic species has been applied at a new electrostatic storage ring to obtain the rate for spontaneous rearrangement of the vinylidene anion to neutral acetylene. The measurement yields a rate of $k_0 = (0.009 \pm 0.006)\ \mathrm{s}^{-1}$, corresponding to a natural lifetime of the vinylidene anion of $\tau_0 \simeq 110$ s.

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Vinylidene and acetylene are constitutional isomers. The acetylene configuration is linear ($D_{\infty h}$ symmetry) with one hydrogen atom positioned at each carbon atom, while the vinylidene configuration is planar (C_{2v} symmetry) with both hydrogen atoms positioned at the same carbon atom. Both configurations are depicted in Fig. 1 together with a schematic energy diagram. The potential energy surface for the electronic ground state of the neutral C_2H_2 system has its global minimum in the acetylene configuration, whereas the global minimum for the electronic ground state of the anion has the vinylidene structure [1–3]. Several theoretical studies have predicted the existence of a neutral vinylidene isomer as a shallow local minimum on the potential energy surface [4–11]. This prediction has been supported by experimental observations [12–15]. It has also been proved experimentally that the vinylidene anion is bound with respect to neutral vinylidene [12,13], while the acetylene anion is unbound with respect to neutral acetylene [16–18].

Several rather different isomerization processes may occur in the vinylidene-acetylene system. These isomerization processes are of fundamental interest, since vinylidene is the simplest molecule rearranging by a 1,2 hydrogen shift, and are also of importance for chemical reactions. Furthermore, vinylidene is the smallest member of the more general family of vinylidenes, $RR'C{=}C{:}$, which are known to play a considerable role as intermediates in organic chemical reactions [19,20]. It is believed that the spontaneous rearrangement from the vinylidene anion to neutral acetylene is very slow for the anion ground state [21]. By using a storage technique, we have performed an experimental study of the decay and rearrangement of the vinylidene anion in its electronic and vibrational ground state.

In order to establish possible decay mechanisms of the vinylidene anion, information about both the neutral and the anionic ground state potential energy surfaces is required. The vertical electron affinity of the vinylidene anion is 0.49 eV [13]. According to *ab initio* calculations of the neutral ground state potential energy surface, neutral vinylidene is about 1.9 eV above neutral acetylene [8–11,22–24] (see Fig. 1). This is supported by an experimentally determined upper bound of 1.9 eV [14]. Hence, the ground state of the vinylidene anion is approximately 1.4 eV above the ground state of neutral acetylene, and the anion can therefore decay to the neutral acetylene isomer through detachment and isomerization. Experimentally, an anion of the acetylene structure has been observed as a resonance at 2.6 eV above neutral acetylene [18]. However, this observed anion is not expected to be in an equilibrium geometry for the system. Instead, the equilibrium geometries of the acetylene anion are the *cis* and *trans* bent structures [3,16]. According to *ab initio* calculations, the lowest state of the acetylene anion (not shown in Fig. 1) has the *trans* geometry and lies 1.7–2.2 eV above neutral acetylene [3,16]. It follows that the vinylidene anion in its vibrational ground state cannot

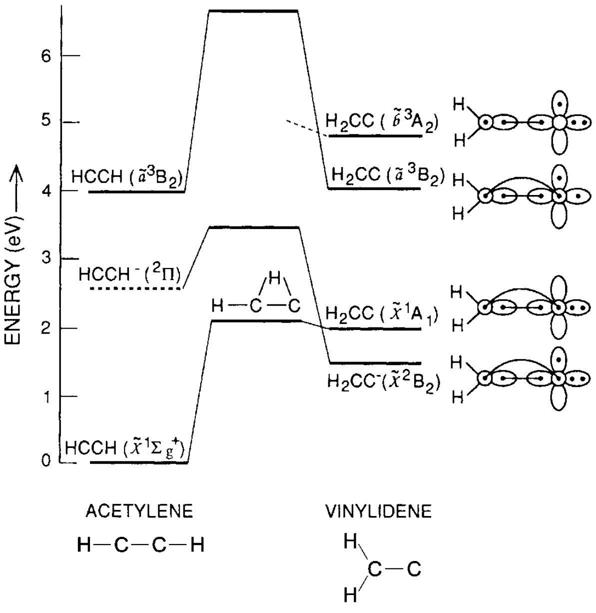

FIG. 1. Energy diagram for the vinylidene-acetylene system (neutral and anionic potential energy surfaces) [13]. Nuclear configurations are shown for acetylene, vinylidene, and the neutral transition state. Orbital diagrams are given for the vinylidene states [13].

isomerize to the acetylene anion. Consequently, the only possible decay mechanism for the vinylidene anion is a rearrangement process involving both isomerization and detachment to neutral acetylene, symbolically written as

$$H_2C{=}C^- \rightarrow HC{\equiv}CH + e^- . \tag{1}$$

Even though the decay process of the vinylidene anion is exothermic by ~1.5 eV, the system is expected to be metastable due to a high barrier against rearrangement. The anionic transition state has been calculated to lie about 2 eV above the vinylidene anion [3]. As shown in Fig. 1, this is a significantly larger energy gap than in the neutral system, in which the transition state is only 0–0.3 eV above neutral vinylidene [4–11]. This difference can be explained by the molecular orbitals. In the isomerization process of the neutrals, the migrating atom moves in the plane from the initial position towards the unoccupied in-plane $p(b_2)$ orbital. In the corresponding process on the anionic potential energy surface, this in-plane orbital is occupied by the additional electron, leading to a repulsive interaction, which forces the migrating hydrogen out of the plane [13]. This is confirmed by the anionic transition state geometry which, according to a calculation, is nonplanar [3].

It is a nontrivial task to determine the actual barrier for this particular isomerization process, since electron emission is involved, but information can be extracted from the neutral and anionic transition states. Since the vinylidene anion during its decay must emit an electron, the energies of the anionic and neutral transition states relative to the vinylidene anion are upper and lower limits on the barrier height. Yet, the actual barrier cannot be determined without knowing when the electron is emitted, and at the present time, the vinylidene anion and its decay are not well understood. With this paper, we hope to stimulate further theoretical progress on this subject.

We present here a measurement of the natural decay rate of the ground state vinylidene anion, H_2CC^-. The experiment was conducted at the new electrostatic ion storage ring ELISA [25], where the decay rate of a stored H_2CC^- beam was measured. However, since the natural decay rate of H_2CC^- was very low, it was impossible to distinguish directly between natural decays and decays caused by collisions with the residual gas. Therefore, the decay rate of the H_2CC^- beam was recorded as a function of pressure in ELISA, and an extrapolation to zero pressure was performed to eliminate collisional contribution to the decay. The zero point of the pressure scale was calibrated by recording the decay rate of a stable beam (O^-) as a function of pressure.

Figure 2 shows a schematic diagram of the setup. O^- was produced in a sputter ion source from a Fe_3O_4 cathode. Inlet of C_2H_4 into the ion source led to the production of vinylidene anions H_2CC^-, presumably from the reaction

$$C_2H_4 + O^- \rightarrow H_2CC^- + H_2O , \tag{2}$$

where O^- produced from sputtering abstracts two hydrogen atoms from the same carbon atom [1,2] delivering an electron in return. The outcome is a water molecule and a vinylidene anion. Any acetylene anions produced in the ion source will decay on a time scale many orders of magnitude shorter than the time scale of this experiment [17]. Ions produced in the ion source were accelerated to 22 keV, and H_2CC^- or O^- beams were selected using a separator magnet and injected into ELISA. Each beam was stored at 22 keV for 50–150 s before being dumped, and background counts of the detector were measured in the subsequent 20 s. This procedure made accurate background subtraction possible. Since all vibrational modes of H_2CC^- are infrared active, the ions quickly relaxed to the vibrational ground state. However, they possessed some rotational excitation, corresponding to the temperature of the ring.

At a given pressure in the ring, the decay rate of the beam was determined from the production rate of neutral particles. Neutrals produced in the first straight section of ELISA were detected by a microchannel plate (MCP) detector, and the count rate on the detector was recorded

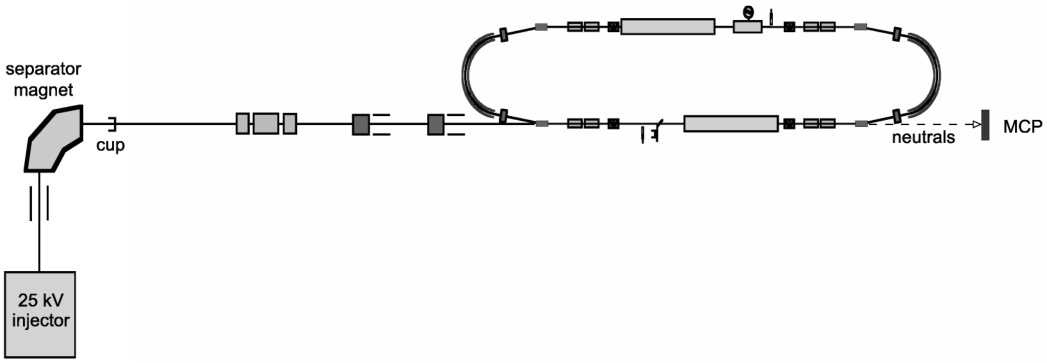

FIG. 2. Schematic diagram of the electrostatic ion storage ring ELISA.

as a function of time after injection. The number of ions in the beam is given by

$$N = \sum_i N_i e^{-k_i t}, \tag{3}$$

where N_i is the number of ions in the state i and k_i is the corresponding decay rate. The count rate on the detector is proportional to the beam decay rate:

$$\frac{dN}{dt} = -\sum_i N_i k_i e^{-k_i t}. \tag{4}$$

When there is only one vibrational state and all rotational levels of this state have the same decay rate k, the decay curve recorded by the detector can be fitted with the function

$$f(t) = Ae^{-kt}, \tag{5}$$

yielding the decay rate k.

The decay rate of H_2CC^- may be written as

$$k(H_2CC^-) = \alpha P + k_0, \tag{6}$$

where k_0 is the natural decay rate of H_2CC^-, P is the pressure in ELISA, and α is a constant of proportionality determined by the ion velocity and the cross section for destruction of H_2CC^- due to collisions with the residual gas. The only existing state of O^- is stable, and with an electron affinity of 1.5 eV blackbody radiation-induced decay of O^- can be neglected. Hence, the collisionless decay rate of O^- is zero, and the decay rate of O^- may be written as

$$k(O^-) = \beta P. \tag{7}$$

The pressure in ELISA was varied above the normal level of $\sim 2 \times 10^{-11}$ mbar by letting in H_2 through a needle valve. H_2 was chosen since this is by far the dominant residual gas component. The destruction cross section may depend on the residual gas composition, and hence inlet of any other gas would introduce a pressure dependence of α and β.

Decay curves of O^- and H_2CC^- were recorded at different pressures in the range $(2-7) \times 10^{-11}$ mbar and fitted with a function of the type given in Eq. (5). A given fit was performed by minimizing χ^2, and goodness of fit was determined as prescribed in [26].

The results of the fits are shown in Fig. 3. For both ions, the decay rate as a function of the measured pressure P_m in ELISA was fitted with a straight line $k = aP_m + b$, yielding the quantities

$$\begin{gathered} a(H_2CC^-) = 0.0175\ \text{s}^{-1}/10^{-11}\ \text{mbar}, \\ b(H_2CC^-) = 0.0092\ \text{s}^{-1}, \\ a(O^-) = 0.0218\ \text{s}^{-1}/10^{-11}\ \text{mbar}, b(O^-) = -0.00016\ \text{s}^{-1}. \end{gathered} \tag{8}$$

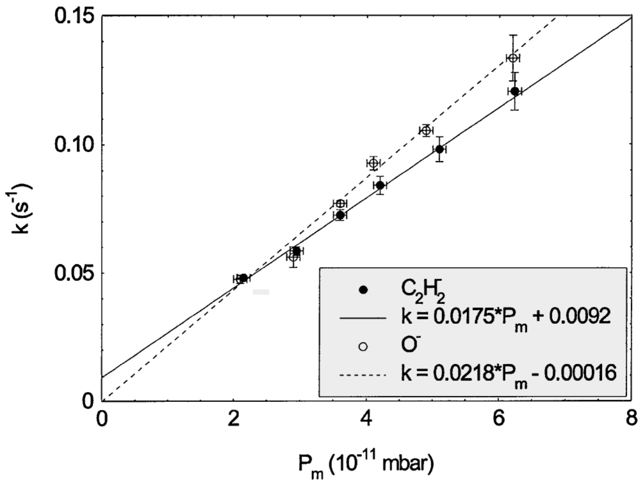

FIG. 3. Decay rate as a function of the measured pressure P_m in ELISA for H_2CC^- (●) and O^- (○). The solid and dashed lines are the linear fits to the H_2CC^- and O^- data, respectively.

The measured pressure P_m, for which $k(O^-) = 0$, defines the true zero point of the pressure scale. Reading of $k(H_2CC^-)$ for this value of P_m yields the collisionless decay rate of H_2CC^-, which in terms of the constants given in Eq. (8) is described by the following equation:

$$k_0 = b(H_2CC^-) - b(O^-)\frac{a(H_2CC^-)}{a(O^-)}. \tag{9}$$

The result of our measurement is

$$k_0 = (0.009 \pm 0.006)\ \text{s}^{-1}. \tag{10}$$

This decay rate is significantly higher than the expected blackbody radiation-induced decay rate, which is estimated to be less than 0.001 s^{-1}. Consequently, the decay rate k_0 given above is ascribed to the natural decay of H_2CC^-, and the corresponding natural lifetime is $\tau_0 \simeq (110^{+180}_{-40})$ s.

The longest (collisionally limited) lifetime of H_2CC^- measured directly was $\tau = (35 \pm 3)$ s. In order to obtain this lifetime, ELISA was cooled down to a temperature of $-40\,^\circ$C. At this temperature, the pressure was reduced to approximately 1×10^{-11} mbar, which was the lower limit determined by gas drifting into ELISA from the injection beam line.

From the measured lifetime of H_2CC^-, it is possible to extract information about the potential barrier through which the system tunnels. A theoretical calculation of the lifetime depends strongly on the potential energy surfaces, and hence a comparison of a theoretical value of the lifetime and the value obtained from this paper will test the quality of calculated potential energy surfaces. A possible way to treat the problem is to perform a full quantum mechanical calculation of relevant parts of the anionic and neutral potential energy surfaces. With knowledge about the potential energy surfaces, the actual reaction pathway can be determined, and finally the lifetime can be calculated using for instance the method of the reaction path Hamiltonian [27]. This method has been used previously to calculate isomerization rates [4,28]. However, the present isomerization process involves detachment, i.e., a transition from an anionic to a neutral potential energy surface must be included in the model. This aspect has not, to our knowledge, been treated previously.

In conclusion, the natural lifetime of the vinylidene anion in its electronic and vibrational ground state has been measured using the storage ring ELISA. Since the lifetime is very sensitive to the shape of the potential energy surfaces involved in the decay process, the measured lifetime may serve to test theoretical potential energy surfaces. Thus, the present measurement provides information about both neutral and anionic potential energy surfaces for the acetylene-vinylidene system. In addition, we hope that our result will contribute to the general understanding of isomerization problems, in particular, isomerization involving a transition between two charge states. Finally, we have demonstrated a technique for measuring long lifetimes of ionic species. This technique may be useful in the future for measuring lifetimes of other long-lived metastable ionic species.

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