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Unimolecular and collision-induced dissociation of Ar_2^+ produced by electron ionization of Ar_2

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Unimolecular and collision-induced dissociation of Ar_2^+ produced by electron-impact ionization of Ar_2 were studied quantitatively with a double-focusing mass spectrometer. The occurrence of the metastable dissociation process $Ar_2^{+*} \rightarrow Ar^+ + Ar$ is interpreted qualitatively in terms of potential-energy curves calculated recently using quantum-mechanical methods.

I. INTRODUCTION

Molecular ions which have dissociation lifetimes in the $\geqslant 10^{-7}$ s time range are usually referred to as metastable ions. There are, in principle, three different dissociation mechanisms possible in these ions: electronic predissociation, tunneling through a (rotational) barrier, or vibrational (statistical) dissociation. Dissociations controlled by statistical mechanisms may be treated within the framework of QET, whereas tunneling and electronic predissociation may be interpreted with use of quantum-mechanical calculations of the respective potential-energy hypersurfaces. In the case of diatomic ions only tunneling and/or electronic predissociation are possible; hence the analysis of metastable dissociations of these systems may provide some information on the respective electronic states.[1-10]

Of the most simple diatomic ions, i.e., rare-gas dimer ions, only for He_2^+ have metastable dissociations been studied[7,10] and compared with theoretical calculations.[7,11,12] Recently, several studies have reported high-quality *ab initio* configuration interaction (CI) calculations on the four states (${}^2\Sigma_u^+$, ${}^2\Pi_g$, ${}^2\Pi_u$, and ${}^2\Sigma_g^+$) of Ar_2^+ arising from the lowest dissociation limit ${}^1S + {}^2P$.[13,14] Since spin-orbit coupling is important for this system, the *ab initio* curves have been modified by these authors[13,14] to include also spin-orbit coupling, yielding six potential-energy curves. Figure 1 shows results of Refs. 13 and 14 which appear to be relevant to the present work. The qualitative behavior of the potential-energy curves obtained from these calculations will be useful in the following discussions.

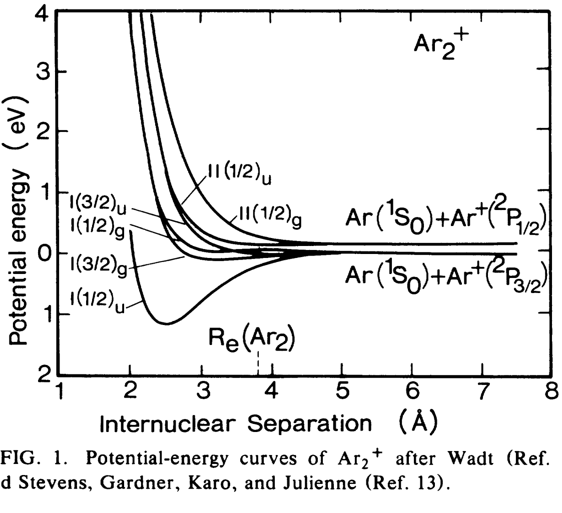

FIG. 1. Potential-energy curves of Ar_2^+ after Wadt (Ref. 14) and Stevens, Gardner, Karo, and Julienne (Ref. 13).

One of these states, the I $(\frac{1}{2})_g$ (following the convention of Hay and Dunning[15]), appears to have only a relative minimum. This, in principle, should give rise to *metastable* Ar_2^+ ions if the I $(\frac{1}{2})_g$ state is populated in one of its rotation-vibrational levels below the maximum of the I $(\frac{1}{2})_g$ potential-energy curve.

These theoretical results stimulated our interest to examine this situation particularly because some of the earlier Ar_2^+ potential-energy curves did not predict all the experimentally observed features of this ion.[16] In the present study measurements of unimolecular and collision-induced dissociation of Ar_2^+ were performed, and the results are found to be consistent with these known theoretical potential curves. Instead of using an ion source in which rare-gas dimer ions are mainly produced by associative ionization and three-body association reactions,[7,10,16,17] we prepare the Ar_2^+ ions by electron-impact ionization of neutral van der Waals dimers via a direct (Franck-Condon) transition.

II. EXPERIMENTAL

The molecular-beam–electron-impact mass spectrometer system has been described in detail elsewhere.[18-22] Only the salient features of the experiment will be discussed in the following. Neutral van der Waals Ar_2 dimers are produced by typically expanding 2000 Torr of argon at room temperature (300 K) through a 10-μm nozzle N (see Fig. 2), although measurements have also been made with seed-

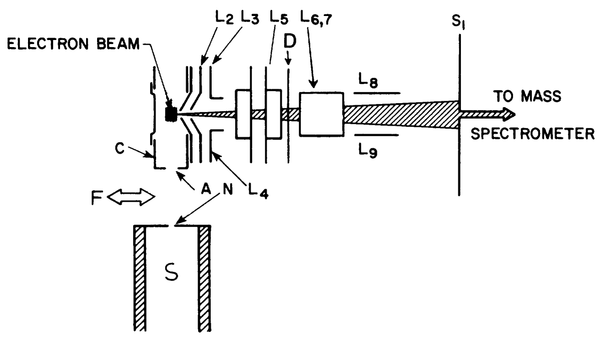

FIG. 2. Schematic view of the molecular-beam-ion-source system. S: stagnation chamber; N: nozzle; F: beam flag; A: aperture; C: collision chamber; L_2: extraction electrodes; L_3 to L_5: ion beam focusing and accelerating electrodes; D: defining aperture; $L_{6,7}$ and $L_{8,9}$: deflection electrodes; S_1: mass spectrometer entrance slit.

ed mixtures and at low temperatures (105 K). The molecular beam [containing several percent Ar_2 (Refs. 18 and 23)] is crossed approximately 4 cm downstream at a right angle by an electron beam (1- to 10-μA current) of 70-eV energy. Ions produced are extracted at a right angle to the ionization region by a weak electric field which penetrates into the collision chamber.[19] This extraction mode combined with a deflection method[19] allows the investigation of processes concerning the molecular beam without interference from reactions in the background gas in the ion source. Special deflection plates in the ion optics between ion source and mass spectrometer (L_8 and L_9 in Fig. 2) serve to move the extracted ion beam across the mass spectrometer entrance slit S_1 (deflection method[19]), thus allowing one to distinguish[18,20,22] Ar_2^+ ions formed by direct ionization of neutral Ar_2 dimers in the beam

$$Ar_2 + e \rightarrow Ar_2^+ + 2e \ , \tag{1}$$

from ions which originate in the stagnant background gas by the associative ionization process

$$\begin{aligned} &Ar + e \rightarrow Ar^* + e \ , \\ &Ar^* + Ar \rightarrow Ar_2^+ + e \ . \end{aligned} \tag{2}$$

Ions passing S_1 are analyzed in a reversed geometry double-focusing sector field mass spectrometer. By decoupling the acceleration and analyzer fields,[24,25] it is possible to investigate the occurrence of dissociations of Ar_2^+ in a specific time window after formation of Ar_2^+ in the ion source by process (1), i.e., between earth slit L_5 and the entrance of the magnetic sector field [(MSF), not shown in Fig. 2]. The time for the Ar_2^+ ions to reach L_5 was calculated to be ~ 3.1 μs.[22] The sampling time (i.e., the time Ar_2^+ ions are traveling through the sampling region between L_5 and MSF) is ~ 4.8 μs.

Prior to this investigation, the general reliability of this experimental setup was tested successfully by studying the metastable decay of N_2O^+ and $C_3H_8^+$.[21,22]

III. RESULTS AND DISCUSSION

In addition to the unimolecular (metastable) dissociation process

$$Ar_2^{+*} \rightarrow Ar^+ + Ar \ , \tag{3}$$

collision-induced dissociation

$$Ar_2^+ + Ar \rightarrow Ar^+ + Ar + Ar \tag{4}$$

occurs in our experimental system as a result of the high background pressure in the ion-source and ion-optics region (typically 4×10^{-5} Torr at a stagnation pressure of 2 atm). In order to separate reactions (3) and (4) the gas density in the field-free region was varied by throttling the pumping speed in the ion source. Figure 3 shows the variation of the parent ion intensity Ar_2^+ and the product ion intensity Ar^+ with gas pressure. In order to account for the change in parent ion intensity (due to scattering, etc.) the intensity ratio $r = i(Ar^+)/i(Ar_2^+)$ is also plotted in Fig. 3. In accordance with previous molecular-beam studies of this type[22,26-29] a linear dependence on pressure is obtained for this ratio, indicating "thin target conditions" for process (4). With use of the thin

$$r = q_c N L \tag{5}$$

target equation (5) with N the number of gas particles per unit volume, L the interaction length between L_5 and S_1 (approximately 8 cm), and q_c the cross section for collision-induced dissociation, it is possible to derive a value for q_c of $\sim 2 \times 10^{-16}$ cm^2 at 3-keV collision energy. This value is of the same order of magnitude as that for the collisional decomposition reactions $C_3H_8^+ \rightarrow C_2H_5^+$ (Ref. 22) and $N_2O^+ \rightarrow NO^+$ (Ref. 21) in their respective parent gases.

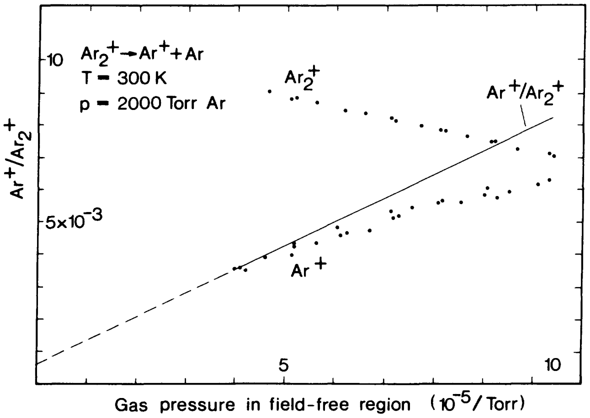

FIG. 3. Pressure dependence of ion intensities (ion count rates of Ar^+ and Ar_2^+ in arbitrary units) for the reaction $Ar_2^+ \rightarrow Ar^+ + Ar$. Also plotted is the ratio of product to parent ion count rate (scale given at left-hand side). The electron energy for the ionization process $Ar_2 + e \rightarrow Ar_2^+$ is 70 eV. The error range for the intercept [i.e., $r = i(Ar^+)/i(Ar_2^+ = 6 \times 10^{-4}$] is difficult to assess. Repeated measurements prove consistently the existence of this metastable dissociation reaction (see also discussion in Refs. 22 and 28).

Extrapolating the intensity ratio $i(Ar^+)/i(Ar_2^+)$ to zero pressure yields a finite intercept (Fig. 3), implying[24] that the product ion Ar^+ is also produced by metastable decay via process (3). Repeated measurements under different experimental conditions (electron current and energy, gas mixture, etc.) establish consistently the existence of this nonzero intercept when Ar_2^+ is formed by electron-impact ionization of the neutral dimer Ar_2. This intercept value gives directly the amount of metastable transitions occurring in the *present* time window (see above) as compared with the parent ion intensity, i.e.,

$$r = i(Ar^+)/i(Ar_2^+) = 6 \times 10^{-4} \ .$$

Stephan and Märk[27,30] have recently reported that the metastable dissociation rate of the Ar_3^+ trimer depends strongly on the stagnation gas temperature. Hence we have also measured the decomposition rate of process (3) at various temperatures between 105 and 300 K. It was found that in the present case the decomposition rate did not change with stagnation temperature within the experimental error bars ($\pm 30\%$). This is in accordance with a preliminary similar result for the metastable dissociation of the ArN_2^+ dimer.[31]

It is interesting to compare the present metastable dissociation process with other known dissociation processes of small cluster ions (see Table I). The CO_2 and NH_3 dimers appear to decompose at least an order of magnitude slower than the Ar and N_2 cluster ions. Illies, Jarrold, and

TABLE I. Metastable dissociations of small cluster ions.

Dissociation process	Metastable-to-precursor ratio	Mechanism	Reference
$Ar_2^+ \rightarrow Ar^+$	6×10^{-4}	Tunneling and/or electronic predissociation	Present
$ArN_2^+ \rightarrow Ar^+$	2.8×10^{-4}	Electronic predissociation and/or tunneling?	Stephan and Märk, 1982 (Ref. 26)
N_2^+	4.4×10^{-4}		
$(N_2)_2^+ \rightarrow N_2^+$	5×10^{-4}	Electronic predissociation and/or tunneling	Stephan, Märk, and Castleman, 1983 (Ref. 29)
$(CO_2)_2^+ \rightarrow CO_2^+$	$< 10^{-4}$	. . .	Futrell, Stephan, and Märk, 1982 and Stephan, Märk, Futrell, and Castleman, 1983 (Ref. 22)
	$\sim 10^{-5}$	Statistical	Illies *et al.*, 1982 (Ref. 32)
$(NH_3)_2^+ \rightarrow NH_3^+$	$< 10^{-4}$	. . .	Futrell *et al.*, 1982 and Stephan *et al.*, 1983 (Ref. 22)
NH_4^+	1×10^{-3}	Statistical?	Futrell *et al.*, 1982 and Stephan *et al.*, 1983 (Ref. 22)

Bowers,[32] who studied the dissociation of $(CO_2)_2^+$, assign this reaction to a statistical decomposition mechanism. There seems to be a reasonable agreement in the decomposition rates of Ar and N_2 cluster ions. In the case of N_4^+ the metastability[29] was explained with the help of *ab initio* potential-energy curves calculated by de Castro, Schaefer, and Pitzer[33] considering rectangle, trapezoid, *T*-shaped, and collinear structures.

The metastable decomposition reaction (3) can be interpreted in terms of tunneling and/or electronic predissociation with use of the calculated potential-energy curves shown in Fig. 1. Also shown in Fig. 1 is the equilibrium internuclear separation [$R_e = 3.76$ Å (Ref. 34)] of the neutral precursor. It can be seen that there exists sufficient Franck-Condon overlap between the neutral Ar_2 and the bound ionic states I $(\frac{1}{2})_u$, I $(\frac{3}{2})_g$, I $(\frac{1}{2})_g$, and II $(\frac{1}{2})_u$. Two of these states, the II $(\frac{1}{2})_u$ and the I $(\frac{1}{2})_g$, are likely candidates for metastable decay via electronic predissociation processes. According to Grössl, Langenwalter, Helm, and Märk,[35] the ion in the II $(\frac{1}{2})_u$ state [well depth of 100 ± 20 meV (Ref. 36)] is unstable for two reasons. The radiative transition II $(\frac{1}{2})_u \rightarrow$ I $(\frac{3}{2})_g$ is dipole allowed ($\sim 1.3\times10^{-4}$ s). In addition, interaction (radial coupling) of the II $(\frac{1}{2})_u$ state with the close-lying I $(\frac{3}{2})_u$ state may lead to metastable predissociation to the lower fine-structure limit $Ar(^1S_0) + Ar^+(^2P_{3/2})$. Moreover, the I $(\frac{1}{2})_g$ ion state can metastably decay by tunneling through the relative barrier or by coupling to the continuum of the I $(\frac{3}{2})_g$ state for $N > 0$. Furthermore, tunneling through rotational barriers may be an additional or alternative mechanism for the observed metastable decay of Ar_2^+.

Note added in proof. It is interesting to point out that Bowers and co-workers (M. T. Bowers, private communication) were not able to observe any metastable reactions of Ar_2^+ produced in a high-pressure mass spectrometer ion source which was cooled to enhance the association products. Conversely, we have recently studied the unimolecular (metastable) and collision-induced dissociations of Ar_2^+ produced by the associative ionization process $Ar + e \rightarrow Ar^* + e$ and $Ar^* + Ar \rightarrow Ar_2^+ + e$. Preliminary results indicate that in this case the intensity ratio $r = i(Ar^+)/i(Ar_2^+)$ is a factor of 100 larger than in the present study.

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