PHYSICAL REVIEW A **69**, 035201 (2004)

Probing potential energy curves of C_2^- by translational energy spectrometry

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(Received 22 October 2003; published 1 March 2004)

We present studies on collision induced dissociation of C_2^- with Ar at an impact energy of 15 keV. The C^- fragment ion kinetic-energy release (KER) distribution is measured and is used to compute the KER in the center of mass (c.m.) frame ($KER_{c.m.}$). We employ the reflection method to deduce an effective repulsive potential-energy curve for the molecular anion that is otherwise difficult to evaluate from quantum computational methods. The nuclear wave packet of the molecular ion in the initial ground state is computed by the semiclassical WKB method using the potential-energy curve of the $^2\Sigma_g^+$ ground electronic state calculated by an *ab initio* quantum computation method. The ground-state nuclear wave packet is reflected on a parametrized repulsive potential-energy curve where the parameters are determined by fitting the measured $KER_{c.m.}$ with the calculated KER distribution.

DOI: 10.1103/PhysRevA.69.035201 PACS number(s): 36.40.Qv, 36.40.Wa

Carbon clusters have been subject of intense research due to the rich variety of structures and dynamics available in these systems [1,2]. Anions of clusters have also been of interest to produce simple doubly charged anions [3]. Being the building block of the carbon clusters, it is important to understand the simple C_2 dimer both to obtain the static properties [4] and reaction dynamics [5]. C_2 has one of the highest electron affinity [6] and has been extensively studied for the possibility of producing the simplest dianions both by electron-impact experiments [3] and also from the laser ablation studies [7]. C_2^- is also important due to the possibility of its presence in the stellar or interstellar medium and is used as a chemical signature for finding the carbonaceous material in the stellar systems [8]. Even though C_2^- has been extensively studied both from theoretical and experimental view points, to the best of our knowledge, there is very little information available on the repulsive potential-energy curves of this system. Undoubtedly the information on the repulsive electronic states is very significant in understanding the reaction dynamics of the system.

We report on experiments to deduce the repulsive potential-energy curve of C_2^- using translational energy spectrometry (TES). TES is now a well established technique to probe the potential-energy surface of molecules [9–13]. The past two decades of work has shown that TES offers stringent test of high level quantum calculations [12], probe dipole forbidden states [14], offers insight into the dynamics of molecular fragmentation [15], and also brings out new phenomena such as “wave-function overlap effects” [16]. While potential-energy surface of the ground state of molecules or of stable excited states can be well determined from emission or excitation spectroscopies [17], it is very difficult to obtain information on repulsive potential-energy surfaces. TES has been used in the past to gain this information on such repulsive states [12,13], but almost always for positive molecular ions.

Collision induced dissociation (CID) of a diatomic molecular cation AB^+ is perceived to be a two-step process [9]. Collision with a neutral atom or molecule results in electronic excitation of the molecule in the first step. If the excitation is to a predissociating state, or a purely repulsive state, the second step of fragmentation occurs. Fragment ions are produced with a release of kinetic energy in the center-of-mass frame ($KER_{c.m.}$) and the released energy is shared between the fragments in the inverse ratio of their masses. TES involves measurement of the fragment ion kinetic energy which reflects the shape of the potential-energy function of the intermediate electronically excited state [12]. In TES, due to energy amplification offered by the vectorial addition of the velocities [18], very small variations of energy (meV) in the c.m. frame can be effectively probed even with moderate energy resolution in the lab frame.

To date most TES experiments have been confined to positive ions. It is relatively easy to produce copious amounts of cations from any atomic or molecular system. Electronic states of positive ions can be easily computed using *ab initio* quantum computation methods. Anions, on the other hand, do not have any of these advantages and as a result the study of anion CID has been very limited. Collisional interaction invariably results in electron detachment, and constitutes the major fraction of inelastic collisions. The negative fragment ion yield is extremely small and is usually undetectable unless the projectile ion beam currents are made commensurately large. Computation of the ground state is itself difficult due to the electron delocalization and strong electron correlations. There is no simple method to perform calculations of the excited electronic energy states of negative ions and repulsive energy states are even more difficult to compute. Also static calculations of the electronic energy at a given internuclear distance are unlikely to give a complete picture as there could be multiple curve crossing leading to autodetachment.

In this paper, we present experimental results on the CID of C_2^-. A momentum analyzed beam of C_2^- negative ions is made to collide with Ar under single-collision conditions and

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the C^- fragment ions that are formed in the interaction are energy analyzed. The KER distribution measured in the lab frame is used to determine $KER_{c.m.}$. We use the GAUSSIAN 98 suite of programs to compute the ground electronic potential-energy state of C_2^- and vibrational energy functions are computed using LEVEL [19]. We use the reflection approximation [12,20] to simulate the fragment ion kinetic energy in the c.m. frame using a parametrized repulsive potential-energy curve. The simulated KER is compared with the experimentally determined $KER_{c.m.}$ and the parameters that determine the repulsive potential-energy curve are optimized by using a least-squares-fitting algorithm. Thus we deduce an effective repulsive potential-energy curve from the experimental measurement that determines the fragmentation dynamics of C_2^-.

The present measurements are conducted using negative-ion beam apparatus that has been described in detail elsewhere [21]. Negative ions of interest are produced in a SNICS (Source of Negative Ions by Cesium Sputtering) source and mass analyzed by a double-focusing 90° magnet, with a mass-energy product of about 10 amu MeV. The mass selected ions are made to interact with an inert gas, such as Ar, in a collision cell under single-collision conditions. Post-collision energy analysis of the forward-scattered ions (with angular resolution of ±0.01°) is carried out using a parallel-plate electrostatic deflector that is remotely scanned by a computerized multichannel analyzer. Ion detection is with a channel electron multiplier coupled to conventional pulse counting electronics. In the present experiments, Cs^+ ions are made to impinge, within the ion source, on a high-purity polycrystalline graphite surface at an energy of 1 keV to produce C_2^- anions. The extracted ions are accelerated to a final energy of 15 keV. We measure the propensity and energy distribution of fragment ion as well as elastically scattered C_2^- anions.

Figure 1 shows the kinetic-energy distribution of the C^- fragment ion obtained from the CID of C_2^- with Ar at a lab-frame kinetic energy of 15 keV. The C_2^- ion beam is made to traverse a collision cell with an Ar pressure of 4×10^{-6} Torr, when the base pressure without Ar is 2×10^{-7} Torr. As shown in Fig. 1 the energy spectrum is devoid of any structure due to the forward- and backward-scattered ions, indicating that the fragmentation is not associated with a large KER [13]. The elastically scattered C_2^- energy distribution is also shown in the inset of Fig. 1. The full width at half maximum (FWHM) of the fragment ion peak is nearly twice as large as the projectile ion peak (C_2^- has a FWHM of 17 eV at 15 keV lab energy and C^- has FWHM of 37 eV). Experiments under different conditions (variations in gas pressure, cathode current, different beam focusing conditions etc) show that the ratio of the projectile and the fragment ion widths, which determine the $KER_{c.m.}$, are highly reproducible and measured uncertainties in the ratio of the projectile and fragment ion width is less than 5%.

The experimental C^- spectrum can be deconvoluted with the instrument function obtained from measuring the C_2^- kinetic-energy spectrum and the kinetic energy in the c.m. frame can be computed using the kinematic equations for forward-scattered particles **(**see Eq. (9) of Ref. [15]**)**. As expected from the above-mentioned arguments, the C^- signal is not very strong, to overcome the numerical problems of deconvolution with a spectrum that is not so smooth we use a Gaussian curve fitted to the measured C^-. The dotted curve in Fig. 1 shows the fitted Gaussian curve used in the deconvolution algorithm [22], which is an excellent approximation of the measured C^- spectrum. Figure 2 shows the $KER_{c.m.}$ computed from the measured spectrum (open circles). As can be seen the KER peaks around zero and has a half width of about 2.2 eV.

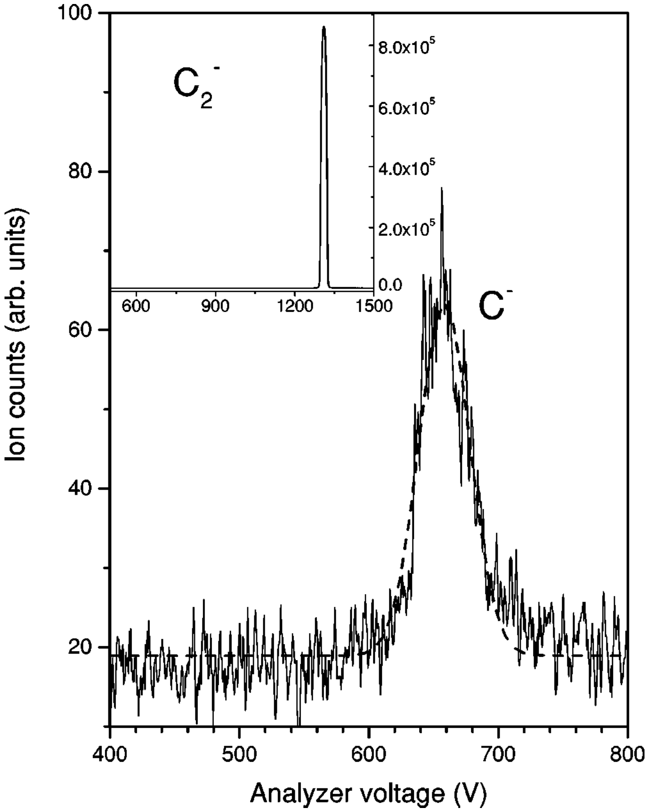

FIG. 1. Lab-frame kinetic-energy release distribution of C^- fragment ion formed in the collision induced dissociation of C_2^- with Ar at an impact energy of 15 keV. The dotted curve shows a Gaussian fit to the spectrum that is used for the deconvolution (see text). Inset shows the C_2^- projectile ion energy spectrum.

As mentioned before, CID is a two-step process and the nature of the potential-energy surface accessed in the collision event is reflected on to the KER distribution of the fragment ion. We have used this earlier to assess the potential-energy states of positive ions computed by quantum computation techniques [12,23] and, more recently, to decipher the dynamics of cluster ion fragmentation [15]. In the reflection method, potential-energy surfaces for the ground and excited electronic states are computed by quantum computational methods. The initial nuclear wave function is computed using semiclassical methods such as the WKB [24]. Transition to the excited state is computed by taking the nuclear wave function for the final state to be a δ function at the turning point, when the final electronic state is purely repulsive. The KER distribution is simulated by reflecting the nuclear wave packet on to the repulsive electronic state. We have shown earlier that the reflection ap-

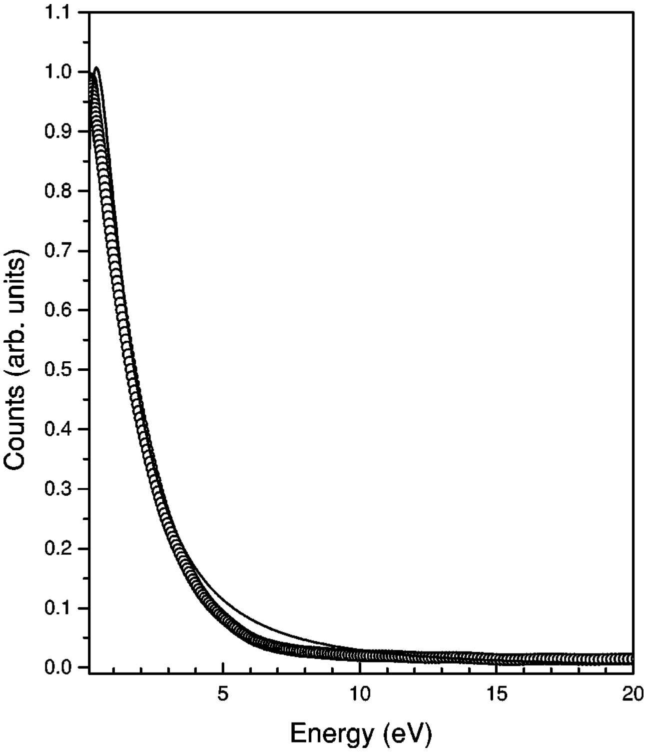

FIG. 2. Kinetic-energy release distribution of the C^- fragment ion in the center-of-mass frame computed from the spectrum measured in the lab frame (open circles). The solid curve shows KER simulated from the reflection of the parametrized repulsive potential-energy curve.

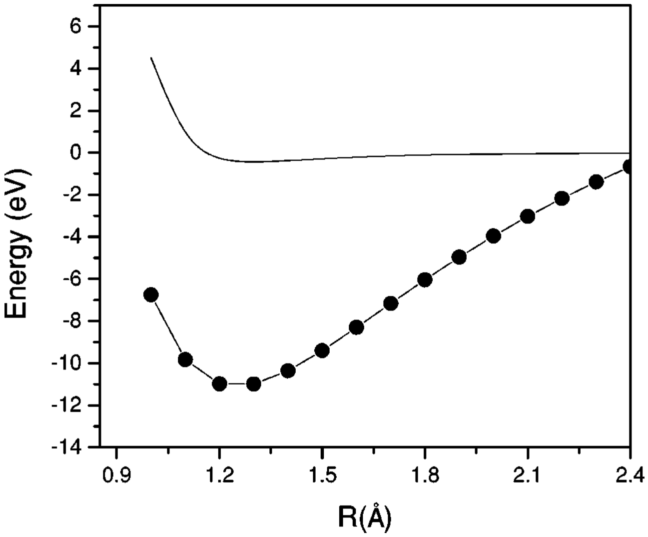

FIG. 3. The line through the solid circles shows the ${}^2\Sigma_g^+$ ground state of the $C_2{}^-$ calculated using QCISD(T) methodology. The solid line shows the effective excited repulsive state of $C_2{}^-$ calculated from the experimental fragment ion energy distribution.

proximation works very well in the case of purely repulsive excited states and the transition function compares very well with those computed using more rigorous time-dependent wave-packet dynamics methods [16].

In the case of negative ions it is very difficult to compute the potential-energy surface for repulsive states. Conventional Hartree-Fock methods are not useful as self-consistent field techniques are inadequate in computing these excited states. Even if one were to use the sophisticated techniques such as the multi-reference configuration interaction [25] there are problems due to large density of states and multiple curve crossings with the Rydberg states in the repulsive electronic energy manifold. To overcome these problems, in this study, we resort to deducing the effective repulsive potential-energy function that is accessed in the collisional dissociation by using the results of our experimental measurements. We assume that the potential energy for the excited repulsive state is represented by a simple Lennard-Jones function

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}, \tag{1}$$

where A and B are the variable parameters that need to be determined. We formulate the repulsive state with initial guess values for A and B, use the reflection approximation with the computed initial nuclear wave function and simulate the KER in the c.m. frame. We compare the simulated spectrum with that obtained from the experimental measurements and use a least-squares-fit method to modify the A and B parameters till a best fit to the experimental spectrum is obtained. We use the Levenberg-Marquadt algorithm [22] for least-squares fitting and the convergence criterion for the mean error as indicated by χ^2 is set to be less than 10^{-4}. The initial ground potential-energy state ${}^2\Sigma_g^+$ is computed using the GAUSSIAN 98 suite of programs with 6-311G** basis function and QCISD(T) methodology [26] to account for the electron correlations. Figure 3 shows the ground state and the deduced repulsive potential-energy curve. The deduced parameters that determine the effective repulsive potential-energy surface of the $C_2{}^-$ molecular ion are $A = 8.5 \pm 0.1$ eV Å^{12}, $B = 4 \pm 0.1$ eV Å^6. The KER spectrum simulated (solid curve) with these best-fit parameters compares well the measured KER distribution as shown in Fig. 2. It is to be noted that the methodology we have used here has an intrinsic assumption that the autodetachment cross-section variation is small for the range of internuclear distances sampled in these experiments.

The conventional method to study the molecular negative ions is by the dissociative electron attachment (DEA) experiments [27]. In these experiments an energy monochromated beam of electrons are made to interact with the neutral molecules and negative fragment ions formed in the dissociative attachment process are detected. It is possible to obtain the information on the repulsive molecular anion states from precise measurement of the fragment ion kinetic energies, though they are mainly used to measure DEA cross sections [28]. As one excites the neutral molecules in these experiments they sample regions of potential-energy surfaces with smaller internuclear distances compared to the experiments presented here. The internuclear distances sampled are larger as the negative ions tend to have a larger bond distances. Since different regions of the excited state potential-energy surface are sampled, these experiments provide complementary information about the dissociation dynamics of excited negative ions. Also, the "energy amplification" available in the TES experiments, which gives the possibility of observing small changes in $\mathrm{KER}_{c.m.}$, is not possible with the electron attachment experiments.

To summarize, we have studied CID of C_2^- with Ar at 15 keV impact energy using translational energy spectrometry. The C^- fragment ion KER distribution measured in the lab frame is used to deduce the $\mathrm{KER}_{c.m.}$. The computed ground-state nuclear wave packet is reflected on a parametrized repulsive potential-energy curve, where the parameters are deduced by fitting the measured $\mathrm{KER}_{c.m.}$ with that of the simulated KER distribution. Thus the reflection method is used to deduce an effective repulsive potential-energy curve for the projectile molecular anion.

We thank Professor D. Mathur and Professor E. Krishnakumar for useful comments and suggestions in reviewing the manuscript.

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