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A tandem mass spectrometry study of the role of electronically excited states in the collision-induced dissociation of the hexafluorobenzene molecular cation

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Abstract

Dissociation of hexafluorobenzene cations via C–F bond cleavage following collisional activation with helium and argon has been studied at 1–4 keV (nominal) laboratory kinetic energies. When hexafluorobenzene cations are formed by 70 eV electrons, the kinetic energy distributions of the fragment ion, $C_6F_5^+$, differ dramatically in that helium collisions proceed via highly endothermic channel whereas argon collisions result in a highly exothermic channel. Both processes are accompanied by a common dissociation pathway, which is nearly thermoneutral. With low energy electron ionization of C_6F_6 and argon collision gas the superelastic peak disappears and an endothermic process analogous to that resulting from helium collisional activation appears. These experimental observations suggest that 70 eV electrons result in the formation of hexafluorobenzene cations in electronically excited state(s) that have radiative lifetimes exceeding 20 μs. The exothermic process corresponds to energy release of ~10 eV into translational mode during the collision and the endothermic process corresponds to transfer of ~17 eV energy from translational to internal modes. Since the threshold for dissociation is 7 eV, we suggest that both endothermic and exothermic channels proceed via the same electronically excited hypersurface. (Int J Mass Spectrom 194 (2000) 171–179) © 2000 Elsevier Science B.V.

Keywords: Tandem mass spectrometry; Collision-induced dissociation; Hexafluorobenzene cation; Electronic excitation; Energy transfer; Kinetic energy release

1. Introduction

Previously reported studies from this laboratory utilizing the crossed molecular beams technique have provided the unequivocal evidence for the formation of long-lived electronically excited states in the electron impact ionization of certain polyatomic molecules and the disposal of this energy in collision-induced dissociation (CID) processes. The ability to measure the interconversion of translational and internal energy and define the angular scattering characteristics of CID in crossed beam experiments have been important factors in establishing the different angular scattering characteristics of ground and electronically excited states for several systems. A partic-

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Dedicated to Professor Jim Morrison on the occasion of his 75th birthday.

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ularly informative example is the CID of the acetone molecular cation [1,2] for which we demonstrated that 70 eV electron ionization forms a significant population (7%–10%) of electronically excited ions in the *A* state with a radiative decay lifetime of the order of 15 ms [3]. Collision of these electronically excited ions with Ar or He atoms at center-of-mass collision energies in the range of 1.3–5 eV triggered an internal conversion to the ground state where rapid dissociation into acetyl ion and methyl radical occurred [1,2]. It was shown that this process is microscopically reversible—i.e. that collision of ground state cations with He and Ar promoted both bound–bound (nondissociative excitation of ground state cations to the electronically excited *A* state) and bound–unbound (excitation of ground state cations to the electronically excited *A*-state level with dissociation occurring on the excited state hypersurface) transitions [4]. These results have been reviewed in recent articles [5,6].

In contrast to the acetone cation, CID dynamics studies of simple hydrocarbons appear to proceed adiabatically on the ground state hypersurface [7]. Collisional activation deposits relatively small energy, primarily in vibrational excitation, into the ground state and energy conversion is nicely correlated with breakdown graphs and interpreted in terms of statistical theories (Rice-Ramsperger-Kassel-Marcus and quasi-equilibrium theory) [8,9]. It appears that nonadiabatic collisional excitation is associated with large gaps in the photoelectron spectrum of the molecule and that vibronic coupling of ground and excited states effectively quenches the participation of excited states in CID. However, too few systems have been studied for us to generalize this observation with confidence.

Crossed-beam measurements are extremely difficult and time consuming and can be carried out only for those systems where relatively intense and stable beams can be sustained for several weeks. (The origin of these limitations is apparent from sensitivity considerations, although collisional excitation in crossed beam experiments typically involves about 2 orders of magnitude lower signals of secondary ions than single beam collision cell and the masking of the detector to achieve moderate angular and energy resolution further drops the detected signal by about three additional powers of ten.) It is therefore of particular interest to us that carefully executed mass analyzed ion kinetic energy spectrometry (MIKES) experiments have also provided evidence for the participation of electronically excited states in CID reactions. In a recent study of the CID of $Cs_4I_3^+$ to $Cs_3I_2^+$ ion in kilovolt laboratory energy range, Boyd and co-workers [10] observed that the kinetic energy of the fragment ions was shifted to lower energies (translationally endothermic) when helium was used as the collision gas and shifted to higher energy (translationally exothermic) when krypton and xenon were used for collisional activation. After careful consideration of various possibilities, it was concluded [10] that the apparently superelastic collisions were best interpreted as internal conversion of an electronically excited state of the $Cs_4I_3^+$ ions on collision with Kr and Xe. They suggested that spin–orbit coupling was readily induced by collision with the heavy rare gases but not by collisions with He.

Recently Lee and Kim [11,12] have reported very similar behavior in a MIKES study of the CID of hexafluorobenzene cation, $C_6F_6^+$, to form $C_6F_5^+ + F$. Specifically they found that CID of 4 keV energy hexafluorobenzene cations on collision with Ar gave a shoulder of intensity at higher translational energy than that expected for unimolecular dissociation of metastable ions (translationally exothermic) whereas He collisions gave a shoulder of intensity which was shifted to lower energy (translationally endothermic), formally exactly analogous to the results reported by Boyd and co-workers [10]. However, Lee and Kim [11,12] suggested that dissociation proceeds via two competing channels with statistical and nonstatistical energy redistributions. The exothermic channel was explained by anisotropic scattering resulting from polarization effects in the interaction of $C_6F_6^+$ with the induced dipole on the collision gas. The higher polarizability of argon versus helium rationalizes such effects being observed for argon collisions and absent in helium collisions.

In view of the results of Boyd and co-workers [10] and our previous crossed-beam dynamics studies at low collision energies, which demonstrated [1,2] uniquely different dissociation dynamics for long-lived excited states, we favored the excited state hypothesis as a possible explanation for CID of hexafluorobenzene cations at high collision energies. To address the different dynamics of the two collision gases we attempted a crossed-beam study of the CID dynamics of this process at low collision energies; unfortunately the small cross section for the reaction precluded our obtaining significant differential cross sections for this reaction. As an alternative approach we have carried out a systematic study of argon and helium CID of high energy $C_6F_6^+$ ions on an instrument very similar to those used by Boyd and co-workers [10] and Lee and Kim [11,12] in their MIKES studies.

2. Experimental

A double focusing reversed geometry mass spectrometer (VG/Micromass ZAB-2F) with a combined electron impact and chemical ionization source and a heated inlet system was used for the present studies. The hexafluorobenzene cations produced in the source were accelerated to 3 keV (nominal) translational energy, mass selected by the magnetic sector, and passed through a collision cell (2 cm path length) where they collide with a neutral gas under single collision conditions. The fragment ions are energy analyzed by the electric sector and detected by a channel electron multiplier. The collision cell is isolated from the ground and floated at some voltage to differentiate dissociation processes occurring inside the cell (CID) from those outside the cell (metastable/unimolecular or delayed dissociations). For CID, the collision gas pressure was maintained such that the primary ion beam attenuated by ~10%. The kinetic energy distributions were collected and signal averaged over sufficient number of scans to give good signal-to-noise ratio.

Energy shifts in CID are determined by measuring the kinetic energy profile of the respective product ions and comparing the location of the centroid of the distribution to that calculated from

$$E_m = (m_f/m_p)\,E_p \tag{1}$$

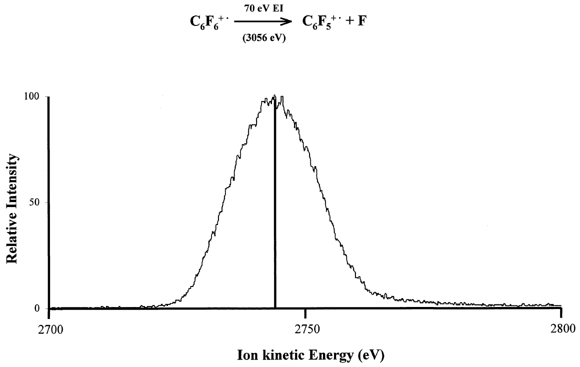

Fig. 1. MIKES spectrum of the unimolecular/metastable dissociation of $C_6F_6^+$ to $C_5F_5^+$. The parent ions were produced by 70 eV electrons and accelerated by 3056 eV kinetic energy for mass analysis by the magnet and dissociation in the field-free region between the magnetic sector and the electric sector. The vertical line shows the location of the peak centroid if there were no transfer of energy.

where m_f and m_p are the masses of the fragment and parent ions and E_p is the kinetic energy of the parent ions. This expression locates the centroids for true unimolecular decay in flight of ions formed by electron impact with sufficient internal energy to undergo decomposition as metastable ions in the field-free region between the mass selecting magnetic and electric sectors of the ZAB 2F mass spectrometer. The linearity and scale of the mass spectrometer were demonstrated to locate true metastables with an accuracy of better than 1 eV by measuring the translational energy of the fragment ions from established metastable decay process of molecular ions such as propane and acetone. The energy analyzer resolution is approximately 2000 for our experiments.

3. Results and discussion

Prior to initiating our study of the CID of

$$C_6F_6^+ + M \rightarrow C_6F_5^+ + F + M \tag{2}$$

where M is the neutral collision target, we carried out a baseline MIKES scan of the region corresponding to metastable unimolecular decay of the parent ions. Fig. 1 illustrates the results of this scan of the electric sector voltage for this process at 3 keV (nominal) energy of the parent ions. The centroid of the peak is located at the position given by Eq. (1) corresponding to the metastable component of reaction (2). Careful examination of the Fig. 1 peak profile (translational energy distribution) reveals a small shoulder on the high energy side. Although this shoulder constitutes a small fraction of the total intensity, it is apparent that this peak does not reflect the Gaussian profile obtained for the parent ion energy distribution under the same experimental conditions.

To investigate the origin of this distortion in the Fig. 1 peak profile we offset the collision cell at 600 V potential with respect to ground to distinguish processes occurring inside the collision cell from those occurring outside the cell (unimolecular decay processes plus any background gas CID occurring along the flight path of the parent ion in the field-free region of the instrument). At this collision energy ions are decelerated to 2400 eV as they enter the collision cell and both undissociated parent ions and any fragment ions formed within the collision cell are accelerated by 600 V when they leave the cell. Consequently any fragment ions formed via reaction (2) occurring inside the cell floating at voltage V_c are found at the nominal energy

$$E_{m*} = (m_f/m_p)E_p + (1 - m_f/m_p)V_c \tag{3}$$

rather than the energy deduced from Eq. (1). Accordingly product ions from CID caused by background gas in the collision cell are offset by 61 V in the laboratory frame.

The results of this experiment are shown in Fig. 2. A fraction of the ion intensity of the order of 60% of the total intensity is shifted to higher kinetic energy and found at the nominal energy predicted by Eq. (2). As shown in Fig. 2, the shifted peak is significantly broader than the unshifted peak and more distorted than the Gaussian shape anticipated for metastable ions. The unshifted peak is slightly narrower than the Fig. 1 kinetic energy distribution and may have the true Gaussian shape predicted for unimolecular decay of a Gaussian primary ion distribution; the partial overlap between the two distributions in Fig. 2 precludes a definitive statement about peak shape of the unimolecular (unshifted) dissociation product ion. The collision cell (shifted) peak evidently results from background gas CID in the cell, whose base pressure is estimated to be approximately 1×10^{-5} Torr taking into account the base pressure in the gas handling system, conductance of the entrance and exit slits of the collision cell and the pumping speeds of the diffusion pumps on both sides of the collision cell. This is about 3 orders of magnitude higher than the baseline pressure in the flight tube. The unshifted peak is estimated from path length considerations to be at least 90% true metastable ions. The shifted peak results from background gas (predominantly nitrogen) CID in the collision cell and we infer that this process is largely responsible for the high energy shoulder on the Fig. 1 energy distribution.

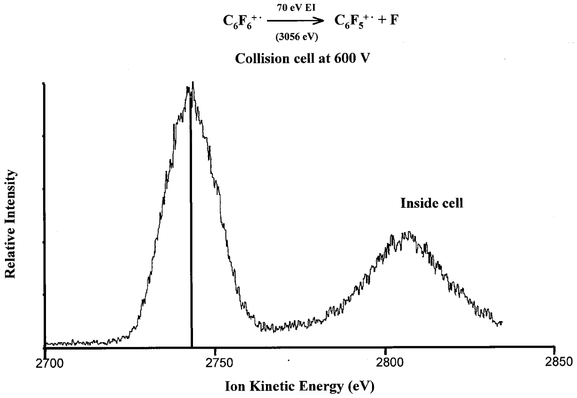

Fig. 2. MIKES spectrum of the unimolecular/metastable dissociation of $C_6F_6^+$ ions to $C_5F_5^+$ ions when the collision cell between the magnetic sector and the electric sector is floated at 600 V. All other experimental conditions were the same as in Fig. 1.

Figs. 3 and 4 show the CID of 3 keV $C_6F_6^+$ ions to $C_6F_5^+$ ions on collision with argon and helium neutrals, respectively. The addition of sufficient collision gas to reduce the parent ion intensity by about 10% increases the ion intensity by more than an order of magnitude and clearly over-rides any contribution from background CID expressed in Fig. 1. Further, the deliberate introduction of collision gas sweeps any background (predominantly nitrogen) gas out of the cell, giving energy distributions which may be clearly identified with the reaction (1) for M = Ar and He in Figs. 3 and 4, respectively. Both of these peaks have

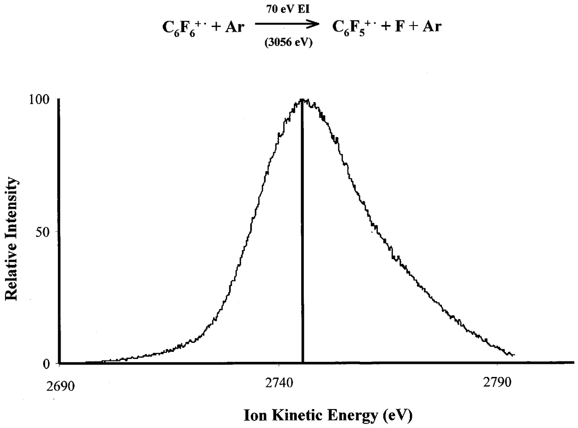

Fig. 3. MIKES spectrum for the CID of $C_6F_6^+$ ions to $C_6F_5^+$ ions on collision with argon neutrals at 3056 eV kinetic energy. The primary ion beam intensity was reduced by ~10% for single collision conditions and the collision cell was grounded. The vertical line marks the location of the peak if there were zero kinetic energy transfer from kinetic to internal modes.

their main peak intensities centered close to zero energy shift [e.g. corresponding to Eq. (1)], indicating that a large fraction of CID with both these gases requires very little conversion of translational into internal energy to initiate the dissociation process. This main peak is thermoneutral within experimental error consistent with our observation of a true metastable (Fig. 2 unshifted peak and Fig. 1 centroid) demonstrates that 70 eV electrons generate a population of molecular ions containing sufficient internal energy to drive this unimolecular decay in the field-free region. The much higher abundance of the peaks in Figs. 3 and 4 (compared with Fig. 1) demonstrates that it results from collisional activation in the collision cell with the respective collision gases.

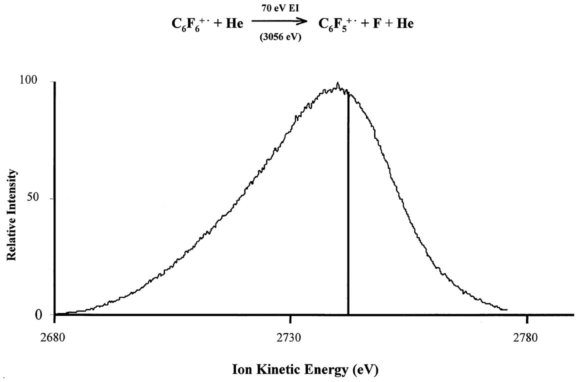

Fig. 4. MIKES spectrum for the CID of $C_6F_6^+$ ions to $C_6F_5^+$ ions on collision with helium neutrals at 3056 eV kinetic energy.

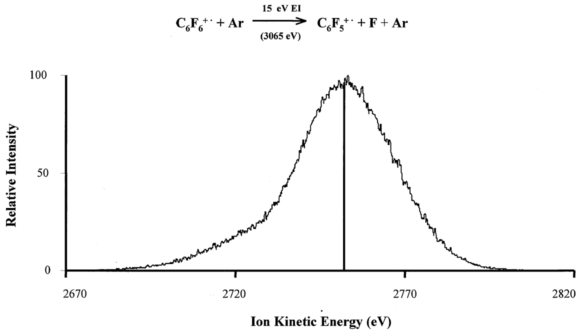

Fig. 5. MIKES spectrum for the CID of $C_6F_6^+$ ions to $C_6F_5^+$ ions on collision with argon neutrals. The primary ions were produced by lowering the electron energy to ~15 eV and extracted from the ion source without any repeller field.

The most interesting feature in Figs. 3 and 4 CID energy distributions is that the shoulder on the argon CID peak is on the high energy side (as in Figs. 1 and 2 for background CID), whereas the helium CID peak has a tail on the low energy side. The latter example is the expected result for a translationally endoergic process. We can describe both CID processes as comprising a thermoneutral main peak [centered at zero energy exchange, Eq. (1)] with a nominally exoergic component for Ar CID and a nominally endoergic component for He CID. These results are in excellent agreement with the data reported by Lee and Kim [11,12].

As stated in Sec. 1 we have previously demonstrated in crossed-beam experiments that translationally exothermic CID processes can serve a useful diagnostic for detecting and characterizing long-lived electronically excited ions. Because the endothermicity of reaction (1) is relatively high (~7 eV [13]) it is relatively straightforward to test the excited state hypothesis by reducing the energy of the ionizing electrons in the ion source of a mass spectrometer. Fig. 5 shows the results for a CID experiment with Ar collision gas where the parent ion beam was generated using ~15 eV energy electrons with both the ion repeller and electron trap voltages set at the source

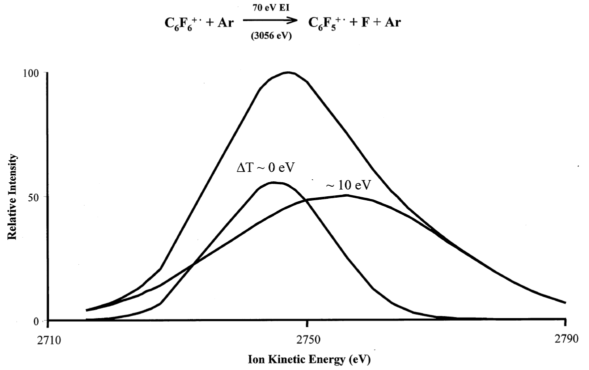

Fig. 6. A fit of two Gaussian peaks to reproduce the composite kinetic energy distribution peak for the CID of $C_6F_6^+$ ions to $C_6F_5^+$ ions on collision with argon neutrals. The exothermic peak is shifted by ~10 eV toward higher kinetic energy whereas the second peak shows nearly zero kinetic energy transfer.

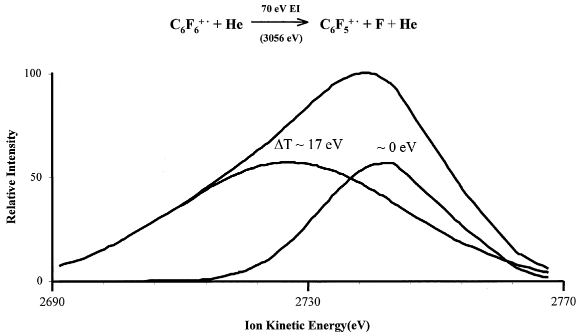

Fig. 7. A fit of two Gaussian peaks to reproduce the composite CID peak for CID with helium neutrals at 3056 eV collision energy. The endothermic peak is shifted to lower energy by ~17 eV kinetic energy whereas the second peak corresponds to nearly zero kinetic energy transfer.

block potential. This experiment demonstrates both that the high energy peak completely disappeared and that CID exhibits endothermic and thermoneutral processes similar to that found for helium collisions. We note that the unimolecular decay process illustrated in Figs. 1 and 2 is decreased in intensity but not completely eliminated with 15 eV electrons. We could not reduce electron energy further because of the instability of parent ion intensities at lower electron energies. Nevertheless, these results clearly confirm the excited state hypothesis for the origin of translationally exothermic CID illustrated in Fig. 3 for molecular ions generated by 70 eV electron impact.

Knowing that CID of $C_6F_6^+$ to $C_6F_5^+$ with these two collision gases proceeds via three energetically distinct pathways, we have deconvoluted the Figs. 3 and 4 kinetic energy distributions assuming that the composite figures are overlapped Gaussian distributions. This deconvolution enables an estimation of energy transfer in both the endoergic and exoergic reaction mechanisms. The results of this deconvolution are shown in Figs. 6 and 7 for Ar and He, respectively. The rather broad Gaussians, which were found, are difficult to interpret with any precision in terms of energy transfer. As indicated in Figs. 6 and 7, we deduce that both peaks have a thermoneutral component (±2 eV) and that the exothermic peak in argon CID corresponds to ~10 ± 3 eV energy transfer from internal modes into translation whereas the endothermic process with helium corresponds to the transfer of ~17 ± 3 eV energy from translation into internal modes.

The width of the distributions shown in Figs. 6 and 7 suggests either a range of energy transfer in CID or relatively high kinetic energy release in the dissociation step, or some combination of both. The kinetic energy release in the dissociation step is amplified in the laboratory frame [14], inevitably resulting in a broad peak in the MIKES spectrum. The magnitude of this effect can be estimated by analyzing the peak broadening in the narrow Gaussian centered at zero kinetic energy shift. Correcting for the primary ion beam energy width using the relationship

$$W_{\mathrm{corr}} = (W_{\mathrm{obs}}^2 - W_{\mathrm{pri}}^2)^{1/2} \tag{4}$$

where W_{obs} and W_{pri} are the widths of the CID peak and the primary ion peak at half heights, respectively, leads to a maximum kinetic energy release of 0.07 and 0.08 eV for argon and helium collisions, respectively, using the relationship [14]

$$T = m_2^2 W_{\mathrm{corr}}^2/(16\, m_1 m_3 E) \tag{5}$$

for ions m_1^+ with kinetic energy E dissociating to m_2^+ and m_3. Similarly, kinetic energy release for the high energy CID process is calculated as 0.28 eV for both helium and argon collision gases. It is quite surprising that it is same in the latter case even though the mechanisms of energy transfer are uniquely different. The only possibility immediately evident is that the energy randomization process in argon collisions is different and possibly nonstatistical.

Within the uncertainties noted previously we can now summarize the energetics of unimolecular dissociation and high energy (keV) CID reaction (1) of hexafluorobenzene cations generated by 70 eV electrons and activated by collision with helium and argon neutrals. First we consider the thermoneutral CID reactions observed for both collision gases. Since it requires about 7 eV to break a C–F bond in the molecular cation, the observation of a true metastable decay process (Figs. 1 and 2) implies a significant fraction of the ions have nearly 7 eV internal total energy. Consequently very little conversion of translational to internal energy is required to drive the dissociation reaction.

The observation of CID with argon (Fig. 6) is translationally exothermic by 10 ± 3 eV combined with the endothermicity of reaction (1) implies a small fraction of the parent ions are internally excited by at least 17 ± 3 eV. The complementary endoergic reaction in helium CID (Fig. 7) transfers ~17 ± 3 eV energy from translational to internal modes to drive the dissociation reaction. The equivalence of energy exchange in both the endoergic and exoergic CID reaction paths suggests that the same state or states may be involved and that the translation $\leftrightarrows$ internal collisional-induced energy exchange process is readily traversed in both directions: the exoergic and endoergic CID reactions. The only logical interpretation for disposal of internal energy of this magnitude is to invoke electronically excited state pathways.

Fig. 8 shows the He II photoelectron spectrum of hexafluorobenzene over the range from the ionization threshold to 27 eV photon energy [15]. The adiabatic ionization energy of hexafluorobenzene is 9.9 eV and there are a number of very well resolved electronic states in this system. It is interesting to note that the photoelectron band at ~27 eV, which matches the energy shifts observed in our CID experiments, has the highest intensity and is well separated from the neighboring band. The intensity of this band identifies it as a favored transition in photon impact (and, by inference, electron impact as well) whereas the large energy gap suggests that internal conversion to the ground state by vibronic coupling is not strong. Similar large energy band gaps and high transition probabilities for generating excited states characterize the acetone and nitromethane cations where we have clearly traced the excited state pathways in CID [1,2,16]. Hexafluorobenzene cations in the excited *B* state undergo a rapid $B \rightarrow X$ transition, which is dipole allowed. For the pathways, which we have described previously, to be valid the transition from the state(s) at 27 eV must be highly forbidden. To our knowledge no one has measured lifetimes for the state or states in this high energy band.

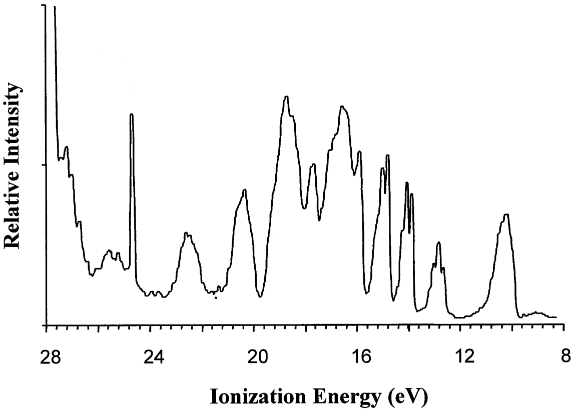

Fig. 8. The photoelectron spectrum of C_6F_6 using He(II) radiation. Taken from [15].

In the absence of any information on the lifetimes of the excited states of hexafluorobenzene cations, the energetics and our experimental observations strongly support the hypothesis that the state(s) at about 27 eV (17 eV internal energy) are the dominant pathway for the CID of the hexafluorobenze cations. When the ion is formed by high energy (e.g. 70 eV) electron impact, collision with Ar atoms triggers internal conversion of the upper state(s) to the ground electronic state hypersurface and dissociation occurs on the lower surface. In the absence of collisions a small fraction of these ions decay spontaneously in the time frame (~20 μs) sampled by our apparatus. This is paralleled by low energy transfer collisions which trigger dissociation by the same pathway with no measureable translational energy transfer. In He CID ground state ions are transferred to the electronically excited surface with transfer of about 17 eV translational energy into internal energy. The ion then dissociates by essentially the same mechanism as those which are already prepared in this state and are manifest in the translationally exoergic process traced by Ar collisions.

Although the near equivalence in the reaction mechanisms traced in unimolecular decay and in CID with the two collision gases is satisfying, the intrinsically different interactions of the excited molecular ion with two rare gases requires further comments. The analogous different dissociation behavior in high energy CID of $Cs_4I_3^+$ ions with helium and argon was rationalized by Boyd and co-workers [10] by invoking important differences in the interaction potential of the cation with the respective rare gases. They asserted that a collision of the excited ion with a neutral having higher polarizability induces curve-crossing resulting in the de-excitation of the ion and release of excess internal energy into translation. The dominance of the electronically excited pathway was rationalized by assuming that the interaction between the neutral and electronically excited ion is greater than that with the ground state.

We can suggest two other possibilities for the present example, as follows. (1) CID involving electronic excitation/de-excitation likely proceeds by a curve-crossing mechanism which is quite sensitive to relative velocity. Since the masses of Ar and He differ by a factor of 10, the relative velocity differs by 3.16 in collisions at the same laboratory energy. This may be sufficient to switch a reaction "on" or "off." (2) The ionization potentials of He and Ar are very different—24.6 and 15.76 eV, respectively. Since the recombination energy of He is relatively close to the highly excited state in the hexafluorobenze cation implicated in the mechanism discussed previously, there is a possibility that the excited state may undergo charge transfer on collision with He but not with Ar. Consequently the open CID channel for helium collisions would be CID of the vibrationally excited ground state ions. The branching ratio for highly vibrationally excited ground states leads predominantly to "thermoneutral" CID reactions whereas less vibrationally excited ground states are pumped to the electronically excited level about 17 eV above the ground state and dissociate as described previously.

4. Conclusions

Our investigation of metastable ions and CID reactions of the hexafluorobenzene cation with He and Ar at 3 keV (LAB) collision energy strongly supports the participation of long-lived isolated electronic states in the lowest energy F-loss channel. The most important experimental observations are the distinctly different mechanisms exhibited by molecular ions formed by low energy (15 eV nominal energy) and high energy (70 eV nominal energy) electrons. This enables a clear distinction between the reactions of highly excited states, most probably located about 17 eV above the ground state, from the reactions of highly vibrationally excited ground state ions and from the reactions of ground state ions with only modest amounts of vibrational energy.

The most intriguing observation—confirming previous reports by Lee and Kim [11,12]—is that CID of hexafluorobenzene cations with Ar leads to product channels with higher translational energy than the metastable while He collisions lead to product channels with lower translational energy that the metastable channel. The existence of the metastable channel (and its differentiation from background gas CID and CID with the gases investigated here) identifies the participation of highly vibrationally excited ions in a CID mechanism, which is translationally thermoneutral within our experimental precision. That electronically excited parent ions (nominally 17 eV internal energy) react with Ar and not with He is rationalized on the basis of details of the curve-crossing mechanism thought to be responsible for CID in the energy regime or on the basis of a competing charge transfer channel with He, which is not substantially accessed in collisions with Ar. The approximate matching of the recombination energy of He with electronically excited hexafluorobenzene cations is the basis of the latter suggestion.

Acknowledgements

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