

Conclusion

The metastability of several energy selected dications has been observed using the TPEsCO ion coincidence technique. Lifetimes were determined from observations within the time window of ~ 0.01 to $2 - 4 \mu\text{s}$, the upper limit being dependent on the time-of-flight of the parent dication.

A band of metastable states is observed for CO_2^{2+} over the energy range ~ 38.7 to 41.3 eV. A comparison of the experimental results with theoretical potential energy surfaces suggests that the metastability is due to slow spin forbidden transitions from the excited singlet states to the ground triplet state of the dication, followed by rapid dissociation of the ground state. The lifetimes observed do not appear to be well modelled by a single lifetime. The lifetimes are most likely to be averages of the lifetimes of all ro-vibrational states excited at each selected internal energy of the dication.

The spectroscopy of CO_2^{2+} has also been investigated with TPEsCO spectra and compared to the TOF-PEPECO results. The double ionisation threshold has been found to be 37.34 ± 0.02 eV, which compares well with previous values. The first two excited states of CO_2^{2+} have also been observed with vibrational resolution. The positions of the electronic and vibrational states have been confirmed by comparison with TOF-PEPECO and theoretical data.

Benzene and deuterio-benzene dications show similar metastable trends in the energy range ~ 26.5 to 27.3 eV, but there is a clear isotope shift of 0.21 ± 0.06 eV. 2,4-hexadiyne, an isomer of benzene, also shows the same trend in metastability, but over the lower energy range ~ 24.0 to 24.5 eV. The energy shift between benzene and 2,4-hexadiyne is close to the difference in the heats of formation for the neutral molecules. All three of these dications have the same lowest dissociation route and it is possible that all the dications dissociate via a common isomeric structure. The lifetime trend of these dications, lower lifetimes at higher energies, suggests that the dissociation occurs by a statistical or tunnelling mechanism. Fits of the RRK statistical model to the lifetime data for these dications gives an indication of the

barrier heights over which dissociation takes place. Barrier heights of ~ 0.7 to 1.7 eV were determined for these three dications, if it is assumed that the metastable decay occurs from common structure for all three isomers.

The hexafluorobenzene dication shows metastable lifetime trends, which are similar to the benzene dications. The lowest energy dissociation route, however, is different. The similarity of the magnitude and trend of the lifetimes for both benzene and hexafluorobenzene dications, although they have different dissociation routes, may indicate that dissociation occurs via a statistical mechanism in both cases. An RRK fit to the lifetime data suggests a barrier height of ~ 1.1 to 2.2 eV, for this dication.

The values determined from the RRK fit are only approximate due to the assumptions made in the RRK model that, for example, all oscillators are harmonic and the decay occurs from a single potential well. In the case of the benzene and deuterio-benzene dications, where rearrangement of the molecular structure of the dication is required prior to dissociation, it is expected that a multiple potential well decay system is likely. The lifetimes values calculated suggest that an average of a range of lifetime events are determined, which supports the multiple well assumption.

If the decay is due to a tunnelling mechanism then it is expected that the potential barriers would be ~ 1 eV higher than those determined in the RRK fit.

Possible reasons for the metastability of the molecular dications, investigated here, have been proposed on the basis of the current data. There is still some uncertainty in the exact method of dissociation, for example, for the larger dications the statistical decay mechanism appears more probable than tunnelling, but the latter cannot be ruled out. For greater insight into molecular dissociation multidimensional potential energy surfaces would help for comparison with experimental data. At the present time, however, such potential energy surfaces remain a theoretical challenge due number of atoms and the large numbers of degrees of freedom in such molecules.

More information could be determined for these dications by performing experiments over a longer run time to improve statistics and by the investigation of a greater number of selected energies over the metastable energy range for a better RRK fitting. The determination of lifetimes over a variety of observation time windows may also give insight into the metastability of the dications and other metastable energy ranges may be observed.

The estimated potential well depths of the $C_6H_6^{2+}$ dications, 0.7 to 1.7 eV, suggests that polyaromatic hydrocarbons, which contain benzene ring structures, could have potential wells of similar depth. These wells would be sufficiently deep to support long-lived PAH^{2+} in the interstellar medium. Therefore, this supports the proposal that the PAH^{2+} may exist with the interstellar medium, as discussed in section 1.3.

A new experiment for the investigation of dissociative electron attachment to molecular radicals is underdevelopment. Preliminary tests for the attachment of electrons to SF_6 and CCl_4 molecules are presented. The results show that further refinement of the apparatus is required to improve the resolution before studying radicals.

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