Dissociative Double Ionization of CO: Dynamics, Energy Levels, and Lifetime

Vandana Sharma, B. Bapat, Jagannath Mondal, M. Hochlaf, Kousik Giri, and N. Sathyamurthy


Downloaded from http://pubs.acs.org on February 19, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML
In a kinematically complete experiment on the dissociative double ionization of CO 2 by electron impact, spontaneous and metastable decay have been observed via the channel CO 2 + → CO + + O +. The metastable decay shows a lifetime of 5.8 ± 1.5 µs. The measured kinetic energy release spectrum of the dissociation shows one broad peak. To understand the observed features, ab initio potential energy surface (PES) for the ground electronic state of CO 2+ was computed using a multireference configuration interaction method and a correlation-consistent polarized-valence quadruple-ζ basis set, for a range of internuclear distances and O—C—O bond angles, and an analytic fit of the PES was obtained. The computed PES clearly indicates the metastability of the dication and yields a barrier height and an asymptotic limit in fair agreement with the reported data. A time-dependent quantum mechanical approach was used to compute the ground vibrational state wave function of CO 2 in its ground electronic state. Assuming a Franck—Condon transition, the same function was taken to be the initial wave function at time $t = 0$ for the time evolution on the fitted PES for the ground electronic state of CO 2+. The autocorrelation function was computed and Fourier transformed to obtain the excitation spectrum. Upon convolution with the instrument resolution function, the kinetic energy release spectrum was obtained, in good agreement with the experimental results, particularly at lower energies. The discrepancies at higher energies are attributed to the noninclusion of the excited states of CO 2+ in the dynamical study.

I. Introduction

The CO 2+ dication has frequently been studied experimentally since it was first observed in 1964. Various methods such as photoionization, electron impact ionization, charge transfer, single-electron capture, Auger spectroscopy, and charge separation mass spectrometry have been designed to study the appearance energy, the excitation energies of higher electronic states, dissociation thresholds, charge separation branching ratios, and lifetimes. The instability of most molecular ions with charges greater than or equal to 2 precludes experimental study of their structure by traditional spectroscopic techniques. Fragment detection and kinetic energy spectroscopy are necessary. A more elaborate method is fragment momentum spectroscopy, which has emerged as the method of choice in the past decade. Theoretical prediction of the instability is a challenge because most strategies for determining the potential energy surface (PES) depend on variational techniques.

The dication of CO 2 was first studied theoretically using the one-electron approximation, self-consistent field (SCF), and restricted configuration interaction (CI) methods for the purpose of calculating the Auger transition intensities and energies. Subsequently, the vertical excitation spectrum was computed by ab initio SCF-CI calculations. But these computations were restricted to the equilibrium geometry of CO 2, and there was no information available on the PES of CO 2+ until Hogreve showed that the ground-state PES of CO 2+ had a local minimum for the collinear symmetric configuration. Unfortunately, his study was restricted to the collinear geometry. Hochlaf et al. extended the study to three dimensions with the main aim of providing insight into the shape of the PES for the electronic ground state of CO 2+ and to deduce its spectrum. The resulting spectral assignment has been published elsewhere. Much of their work was confined to energies up to only 8000–12 000 cm$^{-1}$ above the minimum and not to the region leading to the dissociation of the dication. Therefore, it was decided to extend the ab initio calculations further to geometries leading to CO + + O + in three dimensions. In view of the good agreement between the predicted and the observed spectra in the earlier study, the additional calculations were carried out at the same level of theory used previously, that is, spdf cc-pVQZ/MRCI.

For the purpose of subsequent dynamical studies, an analytic function was fitted to the ab initio PES, and the dissociative dynamics of CO 2+ was investigated using a time-dependent quantum mechanical wave packet approach. Krishnamurthy et al. demonstrated the utility of such an approach to the dissociation dynamics of diatomic cations. More recently, Tarisien et al. showed how the approach could account for the experimentally observed kinetic energy release (KER) spectrum of CO 2+. The method makes use of the fact that the target molecule CO 2 undergoes multiple ionization due to the impact of the fast moving electron in a Franck—Condon manner. What this means is that the stationary state wave function...